



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification : Not classified	A2	(11) International Publication Number: WO 00/41522 (43) International Publication Date: 20 July 2000 (20.07.00)
(21) International Application Number: PCT/US00/00437 (22) International Filing Date: 7 January 2000 (07.01.00) (30) Priority Data: 60/115,379 11 January 1999 (11.01.99) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BETTIOL, Jean-Luc, Philippe [FR/GB]; 8 East Avenue, Benton, Newcastle Upon Tyne NE12 9PH (GB). ZHU, Yong [CN/US]; 4348 Bromyard Avenue, Cincinnati, OH 45241 (US). WELLS, Eric, Christopher [US/US]; 1440 West Kemper Road, Cincinnati, OH 45240 (US). SHOWELL, Michael, Stanford [US/US]; 685 Compton Road, Cincinnati, OH 45231 (US). COVENANTS, Andre, Christian [US/US]; 9696 Humphrye Road, Cincinnati, OH 45242 (US). THOEN, Christiaan, Arthur, Jacques, Kamiel [BE/US]; 8485 Rupp Farm Drive, West Chester, OH 45069 (US). WARD, Glenn, Steven [US/GB]; 3 Willerby Drive, Whitebridge Park, Gosforth, Newcastle Upon Tyne NE3 4HE (GB). SPEED, Lynda,		Anne [US/GB]; 21 Mayfield Road, Gosforth, Newcastle Upon Tyne NE3 4HE (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: CLEANING COMPOSITIONS CONTAINING A MULTI-FUNCTION COMPONENT AND METHOD FOR USING		
(57) Abstract The present invention relates to cleaning compositions comprising a multi-function component that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans, and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof, and methods for using the cleaning compositions for cleaning, especially tough food cleaning, or otherwise removing and/or reducing soils, especially carbohydrate soils, and/or removing or reducing spotting and films, from dishware, cookware and other hard surface substrates.		

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CLEANING COMPOSITIONS CONTAINING
A MULTI-FUNCTION COMPONENT AND METHOD FOR USING

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TECHNICAL FIELD

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The present invention relates to cleaning compositions comprising a multi-function component capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans, and methods for cleaning hard surface substrates, especially dishware, cookware, tableware, etc., by applying such cleaning compositions to the substrates. More specifically, the present invention relates to cleaning compositions that provide tough food cleaning, or otherwise removing and/or reducing soils, especially carbohydrate soils, and/or removing and/or reducing spotting and/or films, from hard surface substrates, especially dishware, cookware, tableware, etc. The cleaning compositions of the present invention and methods of using same, provide enhanced cleaning and improved tough food cleaning and/or removal and/or reduction of spotting and/or films from hard surface substrates relative to amylase-containing detergent compositions without such a multi-function component.

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BACKGROUND OF THE INVENTION

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Detergents used for washing tableware (i.e., glassware, china, silverware, plastic, etc.), dishware, cookware or kitchenware in the home or institution have long been known. Dishwashing in the seventies is reviewed by Mizuno in Vol. 5, Part III of the Surfactant Science Series, Ed. W.G. Cutler and R.C. Davis, Marcel Dekker, N.Y., 1973, incorporated by reference. The particular requirements of cleansing tableware and leaving it in a sanitary, essentially

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stainless, residue-free state has indeed resulted in so many particular compositions that the body of art pertaining thereto is now recognized as quite distinct from other cleansing product art.

Various types of enzymes have long been used in laundry detergents to assist in the removal of certain stains from fabrics. Each class of enzyme (amylase, protease, etc.) generally catalyzes a different chemical reaction. For example, protease enzymes are known for their ability to hydrolyze (break down a compound into two or more simpler compounds) other proteins. This ability has been taken advantage of through the incorporation of naturally occurring or engineered protease enzymes to laundry detergent compositions.

In recent years the use of enzymes has also been investigated for use in automatic dishwashing compositions.

However, consumers continue to experience problems with stain, soil and tough food removal on various substrates, including typical kitchenware surfaces. In particular, formulators have experienced difficulties in formulating detergents which remove carbohydrate soils such as cereal and grain soils, for example, oatmeal, barley, rye, wheat, and rice. Typically, for carbohydrate soil removal, formulators have turned to amylase and hemicellulase enzymes. However, consumers continue to experience problems in removing carbohydrate soils.

WO 95/35382 to Gist-Brocades discloses the use of hemicellulases, such as xylanases, in dishwashing compositions.

Additionally, consumers interest in automatic dishwashing compositions which deliver tough food cleaning is increasing. Cooked-on, baked-on, dried-on and/or burned-on cereals and grains have long been difficult to effectively remove via automatic dishwashing. In addition, consumers now desire less handwashing or pre-washing of dishes and more cleaning ability delivered via the automatic dishwasher.

The prior art fails to teach or suggest the cleaning compositions of the present invention comprising the multi-function component of the present invention.

Accordingly, there is still a need for compositions that provide enhanced and improved tough food cleaning, especially of carbohydrate soils; that provide enhanced and improved tough food cleaning under automatic dishwashing conditions; that provide tough food cleaning via cellulase enzymes designed to deliver such benefits; and that provide removal/reduction of spotting and films from hard surfaces.

SUMMARY OF THE INVENTION

The present invention meets the needs discussed above. The present invention provides cleaning compositions that contain a multi-function component capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans

and 1,4- β -glucans, and methods for cleaning hard surface substrates, especially dishware, cookware, tableware, etc., by applying such cleaning compositions to the substrates.

By the present invention, it has now been surprisingly found that cleaning compositions containing the multi-function component of the present invention, when applied directly to a surface in need of cleaning, such as a carbohydrate soiled surface, provide significantly better cleaning of the surface relative to amylase-containing detergent compositions without such a multi-function component.

The cleaning compositions described herein provide superior removal and/or reduction of soils, especially carbohydrate soils, such as oatmeal, barley, rye, wheat and rice, and/or spotting and films objected to by the consumer from stainless steel and other metals, plastic, ceramic, dishware, cookware, glass, wood, baby bottles, and many other known hard surface substrates, both porous and non-porous.

By "multi-function component" it is meant a component that exhibits or performs more than one function. In the case of the present invention, the multi-function component is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans. With respect to the combinations, by "physically linked" it is meant that distinct, discrete 1,3- β -glucans and 1,4- β -glucans are mixed with each other; by "chemically linked", it is meant that 1,3- β -glucans and 1,4- β -glucans are present in a single molecule (i.e. branched 1,3/1,4- β -glucans, and mixed 1,3/1,4- β -glucans).

By "effective amount" or "soil removal-improving amount" it is meant an enzyme in any amount capable of measurably improving soil removal (especially carbohydrate soils) from the surface, i.e., soiled dishware, cookware, countertop, etc., when it is washed by the consumer, either manually or by an automatic washing machine (laundry or dishwashing). In general, this amount may vary quite widely.

By "tough food cleaning" it is meant the ability to clean cooked-on, burned-on, baked-on or dried-on foods. Examples include burned-on, baked-on and dried-on oatmeal.

By "surface in need of cleaning" it is meant a surface such as tableware, dishware, cookware and other hard surface substrates including but not limited to varieties of stainless steel and other metals, glass, ceramic, baby bottles, wood and plastic that is soiled by any type of soil, preferably a carbohydrate soil, and/or has spots or films.

In accordance with one aspect of the present invention, a cleaning composition, preferably a detergent composition, comprising the multi-function component of the present invention and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof is provided.

In accordance with another aspect of the present invention, a cleaning composition, preferably a detergent composition, comprising the multi-function component of the present

invention, an amylase and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof is provided.

In accordance with yet another aspect of the present invention, a fabric cleaning composition comprising the multi-function component of the present invention, at least about 5% surfactant and at least about 5% builder, at least one other cleaning adjunct material selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof, and optionally, a bleaching agent and/or amylase is provided

--- In accordance with yet another aspect of the present invention, a dishwashing detergent composition comprising:

(a) from about 0.0001% to about 10% by weight of the composition of the multi-function component of the present invention;

(b) from about 0.1% to about 10% by weight of the composition of a low foaming nonionic surfactant; and

(c) optionally, from about 0.5% to about 20% by weight of the composition of a bleaching agent; and

(d) optionally, from about 0.0001% to about 2% by weight of an amylase is provided.

In accordance with still yet another aspect of the present invention, an automatic dishwashing composition comprising:

(a) a tablet body including one or more cleaning adjunct materials; and

(b) a dimple portion including the multi-function component of the present invention;

wherein said dimple portion is attached to said tablet body such that said multi-function component is capable of activation in a wash solution prior to activation of said one or more cleaning adjunct materials of said tablet body is provided.

In accordance with yet another aspect of the present invention, a method for cleaning a surface in need of cleaning is provided. The method comprises contacting the surface in need of cleaning with an effective amount of a cleaning composition containing the multi-function component of the present invention, and optionally an amylase and/or optionally one or more cleaning adjuncts, such that the cleaning composition cleans (e.g., cleans a wide range of soils) the surface.

In accordance with yet another aspect of the present invention, a method for cleaning a dish in need of cleaning comprising contacting the dish with a dishwashing cleaning composition described herein is provided.

In accordance with still yet another aspect of the present invention, a surface cleaned by the methods of the present invention is provided.

Yet another aspect of the present invention is a product comprising a cleaning composition containing the multi-function component of the present invention and a cleaning adjunct material selected from the group consisting of low foaming nonionic surfactants, the product further including instructions for using the cleaning composition to clean surfaces in need of cleaning.

Still yet another aspect of the present invention is a product comprising a cleaning composition containing the multi-function component of the present invention and an amylase and at least one cleaning adjunct material selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof, the product further including instructions for using the cleaning composition to clean surfaces in need of cleaning.

Accordingly, the present invention provides: cleaning compositions that are effective and efficient in cleaning surfaces in need of cleaning; methods of using the cleaning composition to clean such surfaces; surfaces cleaned with the cleaning compositions; and products comprising the cleaning compositions.

All percentages and proportion herein are by weight, and all references cited herein are hereby incorporated by reference, unless otherwise specifically indicated.

DETAILED DESCRIPTION OF THE INVENTION

Multi-function component - Suitable multi-function components for use in the cleaning compositions of the present invention include multi-function components that hydrolyze 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans. Preferred multi-function components in accordance with the present invention are enzymes. More preferred multi-function components in accordance with the present invention are cellulases. Most preferred multi-function components in accordance with the present invention are endoglucanases (EC 3.2.1.4).

One of the top consumer relevant tough soils based on cleaning failure and frequency is oatmeal cereal which contains significant amounts of glucan substrates. Glucan substrates present in the cell wall of cereal meals are very sticky and difficult to remove. The also glue and prevent other soils from being removed. It has been found that the endoglucanase of the present invention can digest glucan polymers that are not degradable by amylases, and further release other soil multi-function components, leading to improved cleaning benefits.

Suitable endoglucanases are described in WO 94/14953 as "Endoglucanase Type IV (otherwise known as Endoglucanase IV or EG IV) and are: (1) encoded at least partially by DNA sequences disclosed in WO 94/14953, which is incorporated herein by reference, in the appended SEQ ID No. 8 and/or SEQ ID No. 19 or a sequence homologous thereto encoding a polypeptide

("a homologue") with 1,3 and 1,4- β -D-glucans activity; and/or (2) enzymes that are immunologically reactive with an antibody raised against a highly purified endoglucanase encoded by the DNA sequence SEQ ID No. 19 and derived from *Aspergillus aculeatus*, CBS 101.43.

5 Endoglucanase IV exhibits a surprisingly high specificity and specific activity towards β -glucan. Endoglucanase IV is described in WO 94/14953 as being capable of degrading cellulose and cellulose derivatives like carboxymethylcellulose and hydroxyethylcellulose, and mixed β -1,3-1,4 glucans like cereal β -glucans.

10 Other endoglucanases for use in the cleaning compositions of the present invention is an endoglucanase (EC 3.2.1.4), which surprisingly catalyzes hydrolysis of internal 1,3- β -D-glycosidic linkages in hemicellulose β -D-glucans, and 1,4- β -D-glycosidic linkages in cellulose, lichenin, and cereal β -D-glucans. The endoglucanase (EC 3.2.1.4) exhibits significant activity on both the 1,3 and 1,4- β -D glycosidic linkages, and does not show substantially greater activity for one over the other. Suitable endoglucanases (EC 3.2.1.4) include, but are not limited to, the
15 endoglucanases (EC 3.2.1.4) described in WO 94/14953 to Novo Nordisk A/S, which is incorporated herein by reference.

Other specific cellulases suitable for the present invention have been described in WO91/17244 wherein single-multi-function component enzymes selected for high specific activity are described and wherein an enzyme capable of degrading cellulose or hemicellulose is
20 disclosed.

Also suitable are the cellulolytic enzymes covered in W095/02675 which describes a detergent composition comprising two cellulase multi-function components : a first cellulase multi-function component having a retaining-type activity and being capable of particulate soil removal and a second cellulase multi-function component having multiple domains comprising at
25 least one non-catalytic domain attached to a catalytic domain and being capable of color clarification wherein at least one of the cellulase multi-function components is a single multi-function component. Said enzymatic detergent composition is capable of providing both sufficient colour clarification and particulate soil removal which, after a limited number of washing cycles, neither damage nor partly degrade the cellulose-containing fabric.

30 A preferred endoglucanase is an endoglucanase which is immunoreactive with an antibody raised against a highly purified ~50kD endoglucanase derived from *Humicola insolens*, DSM 1800, or which is a homologue or derivative of the ~50kD endoglucanase exhibiting cellulase activity; a preferred endoglucanase has the amino acid sequence disclosed in PCT Patent Application No. WO91/17244, or an endoglucanase which is immunoreactive with an
35 antibody raised against a highly purified ~50kD (apparent molecular weight, the amino acid composition corresponds to 45kD with 2n glycosylation sites) endoglucanase derived from

Fusarium oxysporum, DSM 2672, or which is a homologue or derivative of the ~50kD endoglucanase exhibiting cellulase activity; another preferred endoglucanase has the amino acid sequence disclosed in PCT Patent Application No. WO91/17244.

5 A preferred multi-function component is a cellulase, more preferably the endoglucanase having the amino acid sequence disclosed WO95/02675 in the appended SEQ ID NO:3 or in WO91/17244, Fig. 13, or a variant of said endoglucanase having an amino acid sequence being at least 60%, preferably at least 70%, more preferably 75%, more preferably at least 80%, more preferably 85%, especially at least 90% homologous with said sequence. The endoglucanase is produced by *Aspergillus oryzae* after transformation with a plasmid containing the DNA
10 sequence corresponding to the amino acid sequence of the SEQ ID NO:3 described in WO95/02675 and using a Taka promotor and AMG terminator. This endoglucanase may be purified to homogeneity using cationic chromatography and has a pI>9. The calculated-pI is based on the amino acid composition using the PHKa values from Adv. Protein Chem. 17, p. 69-165 (1962) C. Tanford. the molar extinction coefficient is calculated to be 58180.

15 More preferred is the cellulase derived from *Humicola insolens*, DSM 1800, having an approximate molecular weight of about 50 kDa, an iso-electric point of about 5.5 and containing 415 amino acids, such as described in WO95/02675 which is an endoglucanase and has the amino acid sequence disclosed therein in the appended SEQ ID NO:2 or in WO91/17244, Fig. 14A-E, or a variant of said endoglucanase having an amino acid sequence being at least 60%, preferably at
20 least 70%, more preferably 75%, more preferably at least 80%, more preferably 85%, especially at least 90% homologous with said sequence.

Other suitable multi-function components include the cellulases that exhibit endo-1,3(4)- β -glucanase activity as described in PCT Patent Application No. WO 95/31533.

Other suitable specific cellulases are the EGIII cellulases from *Trichoderma*
25 *longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994.

The endoglucanase may be derived or isolated and purified from microorganisms which are known to be capable of producing cellulolytic enzymes, e.g. species of *Humicola*, *Bacillus*, *Trichoderma*, *Fusarium*, *Myceliophthora*, *Phanerochaete*, *Schizophyllum*, *Penicillium*, *Aspergillus* and *Geotricum*. The derived multi-function components may be either homologous or
30 heterologous multi-function components. Preferably, the multi-function components are homologous. However, a heterologous multi-function component which is immunoreactive with an antibody raised against a highly purified cellulase multi-function component possessing the desired property or properties and which heterologous multi-function component is derived from a specific microorganism is also preferred.

Other suitable cellulases are the EGIII from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994, and the cellulases that exhibit endo-1,3(4)- β -glucanase activity described in WO97/44361.

In the present context, the term "homologue" is intended to indicate a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for the endoglucanase enzyme with this amino acid sequence under certain specified conditions (such as presoaking in 5xSSC and prehybridizing for 1 h at about 40°C in a solution of 20% formamide, 5xDenhardt's solution, 50mM sodium phosphate, pH 6.8, and 50 μ g of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 100 μ M ATP for 18 h at about 40°C). The term is intended to include derivatives of the aforementioned sequence obtained by addition of one or more amino acid residues to either or both the C- and N-terminal of the native sequence, substitution of one or more amino acid residues at one or more sites in the native sequence, deletion of one or more amino acid residues at either or both ends of the native amino acid sequence or at one or more sites within the native sequence, or insertion of one or more amino acid residues at one or more sites in the native sequence.

For industrial production of the cellulase preparation herein, however, it is preferred to employ recombinant DNA techniques or other techniques involving adjustments of fermentations or mutation of the micro-organisms involved to ensure overproduction of the desired enzymatic activities. Such methods and techniques are known in the art and may readily be carried out by persons skilled in the art.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimize their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

Amylase - In preferred embodiments of the cleaning compositions of the present invention, an amylase, in addition to the multi-function components described above, is incorporated into the cleaning compositions. A preferred amylase is an α -amylase. The α -amylase is an endoglucosidase (EC 3.2.1.1) which catalyzes the hydrolysis of internal α -glucosidic linkages in starches.

It has been surprisingly found that a cleaning composition containing the endoglucanase (3.2.1.4) of the present invention and an amylase delivers synergistic performance benefits in dish applications. In other words, a cleaning composition containing the endoglucanase (3.2.1.4) of the present invention and the amylase performs significantly better than each single enzyme alone at equal total enzyme levels. Therefore, the combination performs better than the cumulative performance of the enzymes used alone.

The endoglucanase (EC 3.2.1.4) of the invention exhibits different substrate specificity from amylase. α -amylases used in detergent systems is an endoglucosidase (EC 3.2.1.1), which catalyzes hydrolysis of internal α -glucosidic linkages in starches. As discussed above, it has been found that a combination of the endoglucanase (EC 3.2.1.4) of the invention with an amylase, such as the α -amylases described herein, maximizes and optimizes the specific functions of each enzyme in the wash and delivers synergistic benefits in cleaning performance that normally can not be achieved by each single enzyme. With such combinations of the two enzymes at different ratios and levels, a wide range of substrate specificity against different consumer soils and high flexibility toward variety of wash conditions and cost-effectiveness can be achieved that leads to performance robustness in global applications.

Amylases useful in the present invention include, but are not limited to, the amylases described in WO 95/26397 and in WO 96/23873 (Novo). These enzymes are incorporated into cleaning compositions at a level of from about 0.0001%, preferably from about 0.00018%, more preferably from about 0.00024%, most preferably from about 0.05% to about 0.1%, preferably to about 0.060%, more preferably to about 0.048% by weight of the cleaning compositions of pure enzyme.

The amylases for use in the present invention are preferably selected from the group consisting of α -amylase variants.

Suitable α -amylase variants for use in the present invention include, but are not limited to the following α -amylases:

(i) α -amylase characterized by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by Phadebas[®] α -amylase activity assay and/or;

(ii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID No. 1 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 2 and/or;

5 (iii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID No. 2 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 3 and/or;

(iv) α -amylase according to (i) comprising the following amino acid sequence N-terminal: His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp (SEQ ID No. 4) or an α -amylase being at least 80% homologous with the amino acid
10 sequence shown (SEQ ID No. 4) in the N-terminal and/or;

(v) α -amylase according to (i-iv) wherein the α -amylase is obtainable from an alkalophilic *Bacillus* species and/or;

(vi) α -amylase according to (v) wherein the amylase is obtainable from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935 and/or;

15 (vii) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to SEQ ID No. 2, ID No. 3, or ID No. 4 and/or;

(viii) variant of a parent α -amylase, wherein the parent α -amylase (1) has one of the amino acid sequences shown in SEQ ID No. 2, ID No. 3, or ID No. 4, respectively, or (2) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequences, in which variants: (A) at least one amino acid residue of said parent α -amylase has been deleted;
25 and/or (B) at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or (C) at least one amino acid residue has been inserted relative to said parent α -amylase; said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase: increased thermostability; increased stability towards oxidation; reduced Ca ion dependency; increased stability and/or α -amylolytic
30 activity at neutral to relatively high pH values; increased α -amylolytic activity at relatively high temperature; and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by
35 Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a *Bacillus* strain but also an amylase encoded by a DNA sequence isolated from such a *Bacillus* strain and produced in a host organism transformed with the DNA sequence.

5 Multi-function component/Amylase Combination - In the cleaning compositions of the present invention, when the multi-function component and amylase are present, the multi-function component and amylase may be present in the cleaning compositions in any ratio. Preferably, the multi-function component and amylase are present in a ppm ratio of multi-function component to amylase of from about 1:20, more preferably from about 1:10, most
10 preferably from about 1:5 to about 20:1, more preferably to about 10:1, most preferably from about 5:1. It is highly desirable that the multi-function component and amylase are present in a ppm ratio of multi-function component to amylase of from about 1:3 to about 3:1.

Further, the multi-function component and amylase, when present, are preferably present in the cleaning compositions of the present invention at a total enzyme level of from about 0.01
15 ppm, more preferably from about 0.2 ppm, most preferably from about 0.6 ppm to about 50 ppm, more preferably 10 ppm, even more preferably 7 ppm, most preferably 4 ppm. It is highly desirable that the multi-function component and amylase, when present, are present in the cleaning compositions of the present invention at a total enzyme level of from about 0.6 ppm to about 3.0 ppm.

20 CLEANING COMPOSITIONS

The cleaning compositions of the present invention comprise an effective amount of a multi-function component that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans. Preferably, the cleaning compositions further include one or more of the following cleaning
25 adjunct materials selected from the group consisting of: surfactants, solvents, clay, polycarboxylate thickeners, builders, dispersants, other enzymes, bleaches, bleach activators, bleach catalysts, baking soda, carbonates, phosphates, hydrobenzoic acid, dicarboxylic acid, siloxanes, perfumes, water and mixtures thereof. More preferably, the cleaning compositions further include an amylase, preferably an α -amylase, as discussed herein.

30 It has been found that the cleaning compositions of the present invention provide superior tough food cleaning benefits, especially on carbohydrate soils, than cleaning compositions that contain amylase, a leading carbohydrate soil enzyme, without a multi-function component that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans.

35 Preferred cleaning compositions in accordance with the present invention comprise from about 0.0001%, more preferably from about 0.001%, most preferably from about 0.02% to about

10%, more preferably 1%, most preferably 0.2% by weight of the compositions of a pure multi-function component (in other words, when the multi-component is an enzyme, the cleaning composition comprises from about 0.0001% by weight of the composition of the pure enzyme) that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans.

Further, it is desirable that the multi-function component of the present invention is present in the cleaning compositions of the present invention in an amount sufficient to provide from about 0.001 ppm, more preferably 0.01 ppm to about 10 ppm, more preferably 6 ppm, of multi-function component in the wash liquor.

The cleaning compositions can be in a variety of forms including, but not limited to, a liquid, a gel, a foam, a spray, a powder, a particulate, a bar, a granule or a tablet, especially a dimple tablet or multi-layer detergent tablet having both compressed and non-compressed portions.

A more preferred multi-layer detergent tablet comprises: 1) a compressed solid body portion having therein at least one mould in the compressed solid body portion; and 2) at least one non-compressed, non-encapsulating portion mounted in the at least one mould of the compressed solid body portion, having an area of B, the at least one non-compressed, non-encapsulating portion comprising at least one detergent active; wherein the surface area of the detergent tablet, excluding areas of the at least one mould, is A; and preferably, wherein the ratio of B to A is from about 1:50 to 4:1, by area.

Most preferred cleaning compositions of the present invention comprise the multi-function component of the present invention, an amylase, and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants.

In addition to the multi-function component of the present invention, one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, and optionally an amylase, the cleaning compositions of the present invention may include an enzyme cocktail derived from two or more other enzymes, such as other carbohydrases including but not limited to other cellulases, other amylases, hemicellulases, cell-degrading enzymes, and pectin-degrading enzymes, and also proteases, lipases, bleaching enzymes and phospholipid/phosphoprotein degrading enzymes.

The term "cleaning adjunct materials", as used herein, means any liquid, solid or gaseous material selected for the particular type of cleaning composition desired and the form of the product (e.g., liquid; granule; powder; bar; paste; spray; tablet; gel; foam composition), which materials are also preferably compatible with the protease enzyme used in the composition.

5 Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form.

The specific selection of cleaning adjunct materials are readily made by considering the surface, item or fabric to be cleaned, and the desired form of the composition for the cleaning conditions during use (e.g., through the wash detergent use). The term "compatible", as used
10 herein, means the cleaning composition materials do not reduce the proteolytic activity of the protease enzyme to such an extent that the protease is not effective as desired during normal use situations. Examples of suitable cleaning adjunct materials include, but are not limited to, surfactants, builders, bleaches, bleach activators, bleach catalysts, other enzymes, enzyme
15 stabilizing systems, chelants, optical brighteners, soil release polymers, dye transfer agents, dispersants, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, alkalinity sources, solubilizing agents, carriers, processing
20 aids, pigments and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101. Specific cleaning composition materials are exemplified in detail hereinafter.

If the cleaning adjunct materials are not compatible with the protease variant(s) in the cleaning compositions, then suitable methods of keeping the cleaning adjunct materials and the protease variant(s) separate (not in contact with each other) until combination of the two
25 components is appropriate can be used. Suitable methods can be any method known in the art, such as gelcaps, encapsulation, tablets, physical separation, etc.

Preferably an effective amount of one or more protease variants described above are included in compositions useful for cleaning a variety of surfaces in need of proteinaceous stain removal. Such cleaning compositions include detergent compositions for cleaning hard surfaces,
30 unlimited in form (e.g., liquid and granular); detergent compositions for cleaning fabrics, unlimited in form (e.g., granular, liquid and bar formulations); dishwashing compositions (unlimited in form and including both granular and liquid automatic dishwashing); oral cleaning compositions, unlimited in form (e.g., dentifrice, toothpaste and mouthwash formulations); and denture cleaning compositions, unlimited in form (e.g., liquid, tablet).

35 As used herein, "effective amount of protease variant" refers to the quantity of protease variant described hereinbefore necessary to achieve the enzymatic activity necessary in the

specific cleaning composition. Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular variant used, the cleaning application, the specific composition of the cleaning composition, and whether a liquid or dry (e.g., granular, bar) composition is required, and the like.

5 Preferably the cleaning compositions comprise from about 0.0001%, preferably from about 0.001%, more preferably from about 0.01% by weight of the cleaning compositions of one or more protease variants of the present invention, to about 10%, preferably to about 1%, more preferably to about 0.1%. Also preferably the protease variant of the present invention is present in the compositions in an amount sufficient to provide a ratio of mg of active protease per 100
10 grams of composition to ppm theoretical Available O₂ ("AvO₂") from any peroxyacid in the wash liquor, referred to herein as the Enzyme to Bleach ratio (E/B ratio), ranging from about 1:1 to about 20:1. Several examples of various cleaning compositions wherein the protease variants of the present invention may be employed are discussed in further detail below. Also, the cleaning compositions may include from about 1% to about 99.9% by weight of the composition
15 of the cleaning adjunct materials.

As used herein, "cleaning compositions" include hard surface cleaning compositions, dishwashing detergent compositions, oral cleaning compositions, denture cleaning compositions and personal cleansing compositions.

20 The compositions of the present invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other cleaning
25 adjunct materials selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

30 The "compact" form of the cleaning compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not
35 exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the

present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides. A preferred filler salt is sodium sulfate.

Liquid cleaning compositions according to the present invention can also be in a "concentrated form", in such case, the liquid cleaning compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid cleaning composition is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the cleaning composition.

Preferably, the cleaning compositions, especially the dishwashing compositions, comprise phosphate builders and/or bleaching agents.

Cleaning Adjunct Materials

Surfactant System - Deterative surfactants included in the fully-formulated cleaning compositions afforded by the present invention comprise at least about 0.01%, preferably at least about 0.1%, more preferably at least about 1% to preferably about 60%, more preferably to about 35%, most preferably to 30% by weight of cleaning composition depending upon the particular surfactants used and the desired effects.

The deterative surfactant can be nonionic, anionic, ampholytic, zwitterionic, cationic, semi-polar nonionic, and mixtures thereof, nonlimiting examples of which are disclosed in U.S. Patent Nos. 5,707,950 and 5,576,282. Preferred cleaning compositions comprise anionic deterative surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants.

Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the C₁₀-C₁₈ alkyl alkoxy sulfates, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, C₁₂-C₁₈ alpha-sulfonated fatty acid esters, C₁₂-C₁₈ alkyl and alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Examples of suitable nonionic, anionic, cationic, ampholytic, zwitterionic and semi-polar nonionic surfactants are disclosed in U.S. Patent Nos. 5,707,950 and 5,576,282.

Nonionic Surfactants - Particularly preferred surfactants in the preferred automatic dishwashing compositions (ADD) of the present invention are low foaming nonionic surfactants (LFNI).

LFNI may be present in amounts from 0.01% to about 10% by weight, preferably from about 0.1% to about 10%, and most preferably from about 0.25% to about 4%. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxyated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers as described in U.S. Patent Nos. 5,705,464 and 5,710,115. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

Highly preferred ADDs herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound as described in U.S. Patent Nos. 5,705,464 and 5,710,115.

The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 95°F (35°C), more preferably solid at about 77°F (25°C). For ease of manufacture, a preferred LFNI has a melting point between about 77°F (25°C) and about 140°F (60°C), more preferably between about 80°F (26.6°C) and 110°F (43.3°C).

In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C₁₆-C₂₀ alcohol), preferably a C₁₈ alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Highly preferred ADDs herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene,

polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 100%, preferably from about 30% to about 70%, of the total LFNI.

5 Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer
10 surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

 A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and
15 polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

 Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low
20 cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 10°C, for optimum control of sudsing throughout a full range of water temperatures.

 LFNIs which may also be used include those POLY-TERGENT® SLF-18 nonionic surfactants from Olin Corp., and any biodegradable LFNI having the melting point properties
25 discussed hereinabove.

 These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detergent Systems", incorporated by reference herein.

 Preferred are ADD compositions comprising mixed surfactants wherein the sudsing
30 (absent any silicone suds controlling agent) is less than 2 inches, preferably less than 1 inch, as determined by the disclosure below.

 The equipment useful for these measurements are: a Whirlpool Dishwasher (model 900) equipped with clear plexiglass door, IBM computer data collection with Labview and Excel Software, proximity sensor (Newark Corp. - model 95F5203) using SCXI interface, and a plastic
35 ruler.

The data is collected as follows. The proximity sensor is affixed to the bottom dishwasher rack on a metal bracket. The sensor faces downward toward the rotating dishwasher arm on the bottom of the machine (distance approximately 2 cm. from the rotating arm). Each pass of the rotating arm is measured by the proximity sensor and recorded. The pulses recorded by the computer are converted to rotations per minute (RPM) of the bottom arm by counting pulses over a 30 second interval. The rate of the arm rotation is directly proportional to the amount of suds in the machine and in the dishwasher pump (i.e., the more suds produced, the slower the arm rotation).

The plastic ruler is clipped to the bottom rack of the dishwasher and extends to the floor of the machine. At the end of the wash cycle, the height of the suds is measured using the plastic ruler (viewed through the clear door) and recorded as suds height.

The following procedure is followed for evaluating ADD compositions for suds production as well as for evaluating nonionic surfactants for utility. (For separate evaluation of nonionic surfactant, a base ADD formula, such as Cascade powder, is used along with the nonionic surfactants which are added separately in glass vials to the dishwashing machine.)

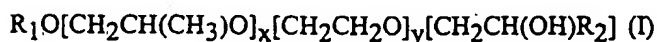
First, the machine is filled with water (adjust water for appropriate temperature and hardness) and proceed through a rinse cycle. The RPM is monitored throughout the cycle (approximately 2 min.) without any ADD product (or surfactants) being added (a quality control check to ensure the machine is functioning properly). As the machine begins to fill for the wash cycle, the water is again adjusted for temperature and hardness, and then the ADD product is added to the bottom of the machine (in the case of separately evaluated surfactants, the ADD base formula is first added to the bottom of the machine then the surfactants are added by placing the surfactant-containing glass vials inverted on the top rack of the machine). The RPM is then monitored throughout the wash cycle. At the end of the wash cycle, the suds height is recorded using the plastic ruler. The machine is again filled with water (adjust water for appropriate temperature and hardness) and runs through another rinse cycle. The RPM is monitored throughout this cycle.

An average RPM is calculated for the 1st rinse, main wash, and final rinse. The % RPM efficiency is then calculated by dividing the average RPM for the test surfactants into the average RPM for the control system (base ADD formulation without the nonionic surfactant). The RPM efficiency and suds height measurements are used to dimension the overall suds profile of the surfactant.

Nonionic ethoxylated alcohol surfactant - The alkyl ethoxylate condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of

alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

End-capped alkyl alkoxyate surfactant - A suitable endcapped alkyl alkoxyate surfactant is the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:



wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 18 carbon atoms; R_2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 26 carbon atoms; x is an integer having an average value of from 0.5 to 1.5, more preferably 1; and y is an integer having a value of at least 15, more preferably at least 20.

Preferably, the surfactant of formula I, at least 10 carbon atoms in the terminal epoxide unit $[CH_2CH(OH)R_2]$. Suitable surfactants of formula I, according to the present invention, are Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

Ether-capped poly(oxyalkylated) alcohols - Preferred surfactants for use herein include ether-capped poly(oxyalkylated) alcohols having the formula:



wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 30, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12, and more preferably 1 to 5.

R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 6 to 22 carbon atoms with 8 to 18 carbon atoms being most preferred. H or a linear aliphatic hydrocarbon radical having from 1 to 2 carbon atoms is most preferred for R^3 . Preferably, x is an integer having an average value of from 1 to 20, more preferably from 6 to 15.

As described above, when, in the preferred embodiments, and x is greater than 2, R^3 may be the same or different. That is, R^3 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^3 may be selected to form ethyleneoxy (EO) or propyleneoxy (PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and

the variation may be much larger with a higher integer value for x and include, for example, multiple (EO) units and a much small number of (PO) units.

Particularly preferred surfactants as described above include those that have a low cloud point of less than 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

Most preferred ether-capped poly(oxyalkylated) alcohol surfactants are those wherein k is 1 and j is 1 so that the surfactants have the formula:



where R^1 , R^2 and R^3 are defined as above and x is an integer with an average value of from 1 to 30, preferably from 1 to 20, and even more preferably from 6 to 18. Most preferred are surfactants wherein R^1 and R^2 range from 9 to 14, R^3 is H forming ethyleneoxy and x ranges from 6 to 15.

The ether-capped poly(oxyalkylated) alcohol surfactants comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

These surfactants exhibit significant improvements in spotting and filming characteristics and removal of greasy soils, when used in conjunction with high cloud point surfactants, relative to conventional surfactants.

Generally speaking, the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention may be produced by reacting an aliphatic alcohol with an epoxide to form an ether which is then reacted with a base to form a second epoxide. The second epoxide is then reacted with an alkoxylated alcohol to form the novel compounds of the present invention. Examples of methods of preparing the ether-capped poly(oxyalkylated) alcohol surfactants are described below:

30 Preparation of C_{12/14} alkyl glycidyl ether - A C_{12/14} fatty alcohol (100.00 g, 0.515 mol.) and tin (IV) chloride (0.58 g, 2.23 mmol, available from Aldrich) are combined in a 500 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C. Epichlorhydrin (47.70 g, 0.515 mol, available from Aldrich) is added dropwise so as to keep the temperature between 60-65 °C. After stirring an additional hour at 60 °C, the mixture is cooled to room temperature. The mixture is treated with a 50% solution of sodium hydroxide (61.80 g, 0.773 mol, 50%) while being stirred

mechanically. After addition is completed, the mixture is heated to 90 °C for 1.5 h, cooled, and filtered with the aid of ethanol. The filtrate is separated and the organic phase is washed with water (100 mL), dried over MgSO₄, filtered, and concentrated. Distillation of the oil at 100-120 °C (0.1 mm Hg) providing the glycidyl ether as an oil.

- 5 Preparation of C_{12/14} alkyl-C_{9/11} ether capped alcohol surfactant - Neodol® 91-8 (20.60 g, 0.0393 mol ethoxylated alcohol available from the Shell chemical Co.) and tin (IV) chloride (0.58 g, 2.23 mmol) are combined in a 250 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C at which point C_{12/14} alkyl glycidyl ether (11.00 g, 0.0393 mol) is
- 10 added dropwise over 15 min. After stirring for 18 h at 60 °C, the mixture is cooled to room temperature and dissolved in an equal portion of dichloromethane. The solution is passed through a 1 inch pad of silica gel while eluting with dichloromethane. The filtrate is concentrated by rotary evaporation and then stripped in a kugelrohr oven (100 °C, 0.5 mm Hg) to yield the surfactant as an oil.

- 15 For more details on these and other suitable nonionic surfactants see U.S. Patent Serial Nos. 60/054,702 (Docket No. 6781P), 60/054,688 (Docket No. 6779P) and 60/057,025 (Docket No. 6780P) all of which are incorporated herein by reference.

- Nonionic ethoxylated/propoxylated fatty alcohol surfactant - The ethoxylated C₆-C₁₈ fatty alcohols and C₆-C₁₈ mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for
- 20 use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of
- 25 propoxylation of from 1 to 10.

- Nonionic EO/PO condensates with propylene glycol - The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from 1500 to 1800 and exhibits water insolubility. Examples of
- 30 compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

- Nonionic EO condensation products with propylene oxide/ethylene diamine adducts - The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of
- 35 these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. Examples of this type of nonionic

surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Mixed Nonionic Surfactant System - In a preferred embodiment of the present invention the detergent tablet comprises a mixed nonionic surfactant system comprising at least one low cloud point nonionic surfactant and at least one high cloud point nonionic surfactant.

"Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed. Vol. 22, pp. 360-379).

As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than 20°C, and most preferably less than 10°C. Typical low cloud point nonionic surfactants include nonionic alkoxyated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers.

Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation) and the ether-capped poly(oxyalkylated) alcohol surfactants.

Nonionic surfactants can optionally contain propylene oxide in an amount up to 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702. Such surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C, preferably greater than 50°C, and more preferably greater than 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from 8 to 20 carbon atoms, with from 6 to 15 moles of ethylene oxide

per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that the high cloud point nonionic surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer
5 hereinbefore) value within the range of from 9 to 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or
10 preferably branched chain or secondary fatty alcohol containing from 6 to 20 carbon atoms (C₆-C₂₀ alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from 6 to 15 moles, preferably from 6 to 12 moles, and most preferably from 6 to 9 moles of
15 ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

In a preferred embodiment the detergent tablet comprising such a mixed surfactant system also comprises an amount of water-soluble salt to provide conductivity in deionised water measured at 25°C greater than 3 milli Siemens/cm, preferably greater than 4 milli Siemens/cm,
20 most preferably greater than 4.5 milli Siemens/cm as described in co-pending GB Patent Application (attorney docket number CM 1573F).

In another preferred embodiment the mixed surfactant system dissolves in water having a hardness of 1.246mmol/L in any suitable cold-fill automatic dishwasher to provide a solution with a surface tension of less than 4 Dynes/cm² at less than 45°C, preferably less than 40°C,
25 most preferably less than 35°C as described in co-pending U.S. Patent Application (attorney docket number 6252).

In another preferred embodiment the high cloud point and low cloud point surfactants of the mixed surfactant system are separated such that one of either the high cloud point or low cloud point surfactants is present in a first matrix and the other is present in a second matrix as
30 described in co-pending U.S. Patent Application (attorney docket number 6252). For the purposes of the present invention, the first matrix may be a first particulate and the second matrix may be a second particulate. A surfactant may be applied to a particulate by any suitable known method, preferably the surfactant is sprayed onto the particulate. In a preferred aspect the first matrix is the compressed portion and the second matrix is the non-compressed portion of the
35 detergent tablet of the present invention. Preferably the low cloud point surfactant is present in

the compressed portion and the high cloud point surfactant is present in the non-compressed portion of the detergent tablet of the present invention.

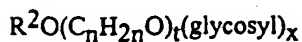
Branched alkyl alkoxylate surfactants - Also suitable are the branched nonionic surfactants disclosed in co-pending U.S. patent application serial number 60/031,917 (Docket No. 6404) all of which is incorporated herein by reference. These branched nonionic surfactants show, some in applications, improved spotting and filming benefits over conventional linear surfactants.

Other Nonionic Surfactants - Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KryoTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides, especially alkylpolyglycosides, disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide.

The preferred alkylpolyglycosides have the formula



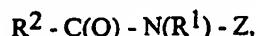
wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof.

Polyhydroxy fatty acid amide surfactants of the formula:



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof can also be used in the present invention. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or C_{16-18} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Anionic Surfactants - Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C_8 - C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil

Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO_3M wherein R preferably is a $\text{C}_{10}\text{-C}_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a $\text{C}_{10}\text{-C}_{20}$ alkyl component, more preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, and M is H^- or a cation, e.g., an alkali metal cation (e.g. sodium,

5 potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of $\text{C}_{12}\text{-C}_{16}$ are preferred for lower wash temperatures (e.g. below about 50°C) and
10 $\text{C}_{16}\text{-C}_{18}$ alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the cleaning compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, $\text{C}_8\text{-C}_{22}$ primary or secondary alkanesulfonates, $\text{C}_8\text{-C}_{24}$
15 olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, $\text{C}_8\text{-C}_{24}$ alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol
ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl
20 isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated $\text{C}_{12}\text{-C}_{18}$ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated $\text{C}_6\text{-C}_{12}$ diesters), acyl sarcosinates, sulfates
of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy
25 carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{-CH}_2\text{COO-M}^+$ wherein R is a $\text{C}_8\text{-C}_{22}$ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and
hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II
30 by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

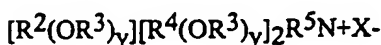
When included therein, the cleaning compositions of the present invention typically comprise from about 1%, preferably from about 3% to about 40%, preferably about 20% by
35 weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein.

Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{18}E(2.25)M$), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{18}E(3.0)M$), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

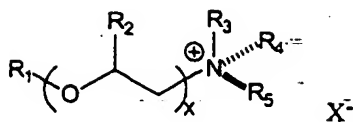
Other Surfactants - The cleaning compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



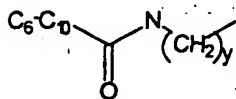
wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



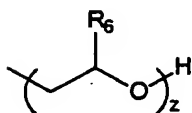
Formula I

wherein R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II):



Formula II

- 5 y is 2-4, preferably 3; wherein R2 is H or a C1-C3 alkyl, wherein x is 0-4, preferably 0-2, most preferably 0, wherein R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,



Formula III

- 15 R6 is C1-C4 and z is 1 or 2; wherein X- is a counterion, preferably a halide, e.g. chloride or methylsulfate.

Preferred quat ammonium surfactants are those as defined in formula I whereby R1 is C8, C10 or mixtures thereof, x=0, R3, R4 = CH3 and R5 = CH2CH2OH.

- 20 Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula (i):



- wherein R1 is C8-C16 alkyl, each of R2, R3 and R4 is independently C1-C4 alkyl, C1-C4 hydroxy alkyl, benzyl, and -(C2H4O)xH where x has a value from 2 to 5, and X is an anion. Not more than one of R2, R3 or R4 should be benzyl. The preferred alkyl chain length for R1 is C12-C15 particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R2R3 and R4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulfate, acetate and phosphate.
- 30

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

When included therein, the cleaning compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 25%, preferably to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

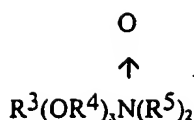
When included therein, the cleaning compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the cleaning compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

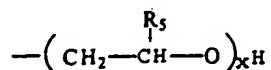
These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such semi-polar nonionic surfactants.

The cleaning compositions of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain or $\text{R}_4\text{X}(\text{CH}_2)_n$, X is $-\text{O}-$, $-\text{C}(\text{O})\text{NH}-$ or $-\text{NH}-$, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

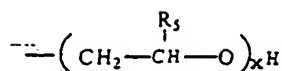
Preferred amines according to the formula herein above are n -alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C_8 - C_{10} oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

Suitable tertiary amines for use herein include tertiary amines having the formula $\text{R}_1\text{R}_2\text{R}_3\text{N}$ wherein R_1 and R_2 are C_1 - C_8 alkyl chains or



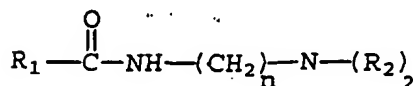
R_3 is either a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain, or R_3 is $\text{R}_4\text{X}(\text{CH}_2)_n$, whereby X is $-\text{O}-$, $-\text{C}(\text{O})\text{NH}-$ or $-\text{NH}-$, R_4 is a C_4 - C_{12} , n is between 1 to 5, preferably 2-3. R_5 is H or C_1 - C_2 alkyl and x is between 1 to 6. R_3 and R_4 may be linear or branched; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $\text{R}_1\text{R}_2\text{R}_3\text{N}$ where R_1 is a C_6 - C_{12} alkyl chain, R_2 and R_3 are C_1 - C_3 alkyl or



where R₅ is H or CH₃ and x = 1-2.

Also preferred are the amidoamines of the formula:



wherein R₁ is C₆-C₁₂ alkyl; n is 2-4, preferably n is 3; R₂ and R₃ is C₁-C₄.

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyl-dimethylamine, C8-10 amidopropyl-dimethylamine and C10 amidopropyl-dimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyl-dimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Bleaching System - The cleaning compositions of the present invention preferably comprise a bleaching system. Bleaching systems typically comprise a "bleaching agent" (source of hydrogen peroxide) and an "initiator" or "catalyst". When present, bleaching agents will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

Bleaching System - The cleaning compositions of the present invention preferably comprise a bleaching system. Bleaching systems typically comprise a "bleaching agent" (source of hydrogen peroxide) and an "initiator" or "catalyst". When present, bleaching agents will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

Bleaching Agents - Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley &

Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions which comprise enzymes.

(a) Bleach Activators - Preferably, the peroxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C₁₀-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C₈-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, dodecanoyloxybenzenesulphonate (LOBS or C₁₂-OBS), 10-undecenoyloxybenzenesulfonate

(UDOBs or C₁₁-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564, all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

Quaternary substituted bleach activators may also be included. The present cleaning compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723 Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety $-C(O)OC(R^1)=N-$.

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl

caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639 Willey et al., issued April 2, 1996 incorporated herein by reference).

(b) Organic Peroxides, especially Diacyl Peroxides - These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

(c) Metal-containing Bleach Catalysts - The present invention compositions and methods may utilize metal-containing bleach catalysts that are effective for use in bleaching compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. 4,430,243 Bragg, issued February 2, 1982.

Manganese Metal Complexes - If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Patent Nos. 5,576,282; 5,246,621; 5,244,594; 5,194,416; and 5,114,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Patent Nos. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. Patent Nos. 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Cobalt Metal Complexes - Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{Ty}$, wherein "OAc" represents an acetate moiety and "Ty" is an anion, and especially cobalt pentaamine acetate chloride, $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as

[Co(NH₃)₅OAc](OAc)₂; [Co(NH₃)₅OAc](PF₆)₂; [Co(NH₃)₅OAc](SO₄); [Co(NH₃)₅OAc](BF₄)₂; and [Co(NH₃)₅OAc](NO₃)₂ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; in the Tobe article and the references cited therein; and in U.S. Patent 4,810,410; J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

Transition Metal Complexes of Macropolycyclic Rigid Ligands - Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL" in discussion below. The amount used is a catalytically effective amount, suitably about 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

Suitable transition metals e.g., Mn are illustrated hereinafter. "Macropolycyclic" means a MRL is both a macrocycle and is polycyclic. "Polycyclic" means at least bicyclic. The term "rigid" as used herein includes "having a superstructure" and "cross-bridged". "Rigid" has been defined as the constrained converse of flexibility: see D.H. Busch., Chemical Reviews, (1993), 93, 847-860, incorporated by reference. More particularly, "rigid" as used herein means that the MRL must be determinably more rigid than a macrocycle ("parent macrocycle") which is otherwise identical (having the same ring size and type and number of atoms in the main ring) but lacking a superstructure (especially linking moieties or, preferably cross-bridging moieties) found in the MRL's. In determining the comparative rigidity of macrocycles with and without superstructures, the practitioner will use the free form (not the metal-bound form) of the macrocycles. Rigidity is well-known to be useful in comparing macrocycles; suitable tools for determining, measuring or comparing rigidity include computational methods (see, for example, Zimmer, Chemical Reviews, (1995), 95(38), 2629-2648 or Hancock et al., Inorganica Chimica Acta, (1989), 164, 73-84.

Preferred MRL's herein are a special type of ultra-rigid ligand which is cross-bridged. A "cross-bridge" is nonlimitingly illustrated in 1.11 hereinbelow. In 1.11, the cross-bridge is a -CH₂CH₂- moiety. It bridges N¹ and N⁸ in the illustrative structure. By comparison, a "same-side" bridge, for example if one were to be introduced across N¹ and N¹² in 1.11, would not be sufficient to constitute a "cross-bridge" and accordingly would not be preferred.

Suitable metals in the rigid ligand complexes include Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium.

More generally, the MRL's (and the corresponding transition-metal catalysts) herein suitably comprise:

- (a) at least one macrocycle main ring comprising four or more heteroatoms; and
- (b) a covalently connected non-metal superstructure capable of increasing the rigidity of the macrocycle, preferably selected from
 - (i) a bridging superstructure, such as a linking moiety;
 - (ii) a cross-bridging superstructure, such as a cross-bridging linking moiety; and
 - (iii) combinations thereof.

The term "superstructure" is used herein as defined in the literature by Busch et al., see, for example, articles by Busch in "Chemical Reviews".

Preferred superstructures herein not only enhance the rigidity of the parent macrocycle, but also favor folding of the macrocycle so that it co-ordinates to a metal in a cleft. Suitable superstructures can be remarkably simple, for example a linking moiety such as any of those illustrated in Fig. 1 and Fig. 2 below, can be used.

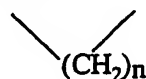


Fig. 1

wherein n is an integer, for example from 2 to 8, preferably less than 6, typically 2 to 4, or

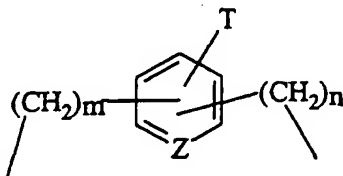


Fig. 2

wherein m and n are integers from about 1 to 8, more preferably from 1 to 3; Z is N or CH; and T is a compatible substituent, for example H, alkyl, trialkylammonium, halogen, nitro, sulfonate, or the like. The aromatic ring in 1.10 can be replaced by a saturated ring, in which the atom in Z connecting into the ring can contain N, O, S or C.

Suitable MRL's are further nonlimitingly illustrated by the following compound:

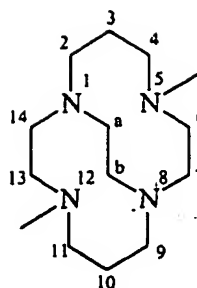


Fig. 3

This is a MRL in accordance with the invention which is a highly preferred, cross-bridged, methyl-substituted (all nitrogen atoms tertiary) derivative of cyclam. Formally, this ligand is named 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane using the extended von Baeyer system. See "A Guide to IUPAC Nomenclature of Organic Compounds: Recommendations 1993", R. Panico, W.H. Powell and J-C Richer (Eds.), Blackwell Scientific Publications, Boston, 1993; see especially section R-2.4.2.1.

Transition-metal bleach catalysts of Macrocyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or cleaning uses, and non-limitingly illustrated by any of the following:

- Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
- 15 Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
Hexafluorophosphate
- Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)
Hexafluorophosphate
- Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Tetrafluoroborate
- 20 Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)
Hexafluorophosphate
- Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane Manganese(II)
- Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
- Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)
- 25 Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)
- Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II).

As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm,

and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the bleaching compositions.

(d) Other Bleach Catalysts - The compositions herein may comprise one or more other bleach catalysts. Preferred bleach catalysts are zwitterionic bleach catalysts, which are described in U.S. Patent No. 5,576,282 (especially 3-(3,4-dihydroisoquinolinium) propane sulfonate. Other bleach catalysts include cationic bleach catalysts are described in U.S. Patent Nos. 5,360,569, 5,442,066, 5,478,357, 5,370,826, 5,482,515, 5,550,256, and WO 95/13351, WO 95/13352, and WO 95/13353.

Also suitable as bleaching agents are preformed peracids, such as phthalimido-peroxycaproic acid ("PAP"). See for example U.S. Patent Nos. 5,487,818, 5,310,934, 5,246,620, 5,279,757 and 5,132,431.

15 Controlled rate of release

The detergent tablet may be provided with a way for controlling the rate of release of bleaching agent, particularly oxygen bleach to the wash solution.

The controlling of the rate of release of the bleach may provide for controlled release of peroxide species to the wash solution. This could, for example, include controlling the release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable ways of controlled release of the bleaching agent can include confining the bleach to either the compressed or non-compressed, non-encapsulating portions. Where more than one non-compressed, non-encapsulating portions are present, the bleach may be confined to the first and/or second and/or optional subsequent non-compressed, non-encapsulating portions.

Another way for controlling the rate of release of bleach may be by coating the bleach with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates, silicates and carbonates, including calcium carbonate and silicas.

A preferred coating material, particularly for an inorganic perhydrate salt bleach source, comprises sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be

5 included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10} - C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15} - C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of

10 ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5×10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with

15 ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10} - C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10} - C_{20} mono- and

20 diglycerol ethers and also the C_{10} - C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred

25 agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other ways of providing the required controlled release include altering the physical

30 characteristics of the bleach to control its solubility and rate of release. Suitable ways could include compression, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the

35 particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

Additional ways for providing controlled release include the suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

- 5 Optional Detergent Enzymes - The detergent and cleaning compositions herein may also optionally contain one or more types of detergent enzymes. Such enzymes can include other proteases, amylases, cellulases and lipases. Such materials are known in the art and are commercially available under such trademarks as . They may be incorporated into the non-aqueous liquid detergent compositions herein in the form of suspensions, "marumes" or "prills".
- 10 Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP." Suitable enzymes and levels of use are described in U.S. Pat. No. 5,576,282, 5,705,464 and 5,710,115.

- Enzymes added to the compositions herein in the form of conventional enzyme prills are
- 15 especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus,
- 20 compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

However, enzymes added to the compositions herein may be in the form of granulates, preferably T-granulates.

- "Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing
- 25 or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though
- 30 more and more bleach compatible though successive improvements, have a remaining degree of bleach deactivation susceptibility.

- Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipxygenases, ligninases,
- 35 pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and known amylases, or mixtures thereof.

Examples of such suitable enzymes are disclosed in U.S. Patent Nos. 5,705,464, 5,710,115, 5,576,282, 5,728,671 and 5,707,950

The cellulases useful in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801 to Genencor. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Cellulases, when present, are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of pure enzyme by weight of the cleaning composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Suitable peroxidases and peroxidase-containing detergent compositions are disclosed, for example, in U.S. Patent Nos. 5,705,464, 5,710,115, 5,576,282, 5,728,671 and 5,707,950, PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxasine 10-

Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

- 5 Said peroxidases are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of pure enzyme by weight of the cleaning composition.

Enzymatic systems may be used as bleaching agents. The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing
10 process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other preferred enzymes that can be included in the cleaning compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as
15 disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*,
20 e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo) which
25 have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to
30 cleaning compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

Lipases and/or cutinases, when present, are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of pure enzyme by weight of the cleaning composition.

35 In addition to the above referenced lipases, phospholipases may be incorporated into the cleaning compositions of the present invention. Nonlimiting examples of suitable phospholipases

included: EC 3.1.1.32 Phospholipase A1; EC 3.1.1.4 Phospholipase A2; EC 3.1.1.5 Lysophospholipase; EC 3.1.4.3 Phospholipase C; EC 3.1.4.4. Phospholipase D. Commercially available phospholipases include LECITASE® from Novo Nordisk A/S of Denmark and Phospholipase A2 from Sigma. When phospholipases are included in the compositions of the present invention, it is preferred that amylases are also included. Without desiring to be bound by theory, it is believed that the combined action of the phospholipase and amylase provide substantive stain removal, especially on greasy/oily, starchy and highly colored stains and soils. Preferably, the phospholipase and amylase, when present, are incorporated into the compositions of the present invention at a pure enzyme weight ratio between 4500:1 and 1:5, more preferably between 50:1 and 1:1.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which Lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase as described in U.S. Patent No. 5,677,272, and WO95/10591. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997 and PCT International Application Serial No. PCT/IB98/00853).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP[®] described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Particularly useful proteases are described in PCT publications: WO 95/30010; WO 95/30011; and WO 95/29979. Suitable proteases are commercially available as ESPERASE[®], ALCALASE[®], DURAZYM[®], SAVINASE[®], EVERLASE[®] and KANNAASE[®] all from Novo Nordisk A/S of Denmark, and as MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] all from Genencor International (formerly Gist-Brocades of The Netherlands).

Such proteolytic enzymes, when present, are incorporated in the cleaning compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597 describes cleaning compositions which incorporate mutant amylases. See also WO95/10603. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314 and WO96/05295, Genencor, and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603. Also suitable are amylases described in EP 277 216.

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases: α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

Such amylolytic enzymes, when present, are incorporated in the cleaning compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, 5 bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimize their performance efficiency in the laundry detergent and/or fabric care compositions of 10 the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the 15 case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

20 These optional detergent enzymes, when present, are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of pure enzyme by weight of the cleaning composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

25 Other suitable detergent ingredients that can be added are enzyme oxidation scavengers. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 and WO 9307260 to Genencor International, WO 8908694, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in 30 U.S. 4,101,457, and in U.S. 4,507,219. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868.

Enzyme Stabilizers - Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, EP 199,405 and EP 200,586. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A 35 useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532. The enzymes employed herein can be stabilized by the presence of water-soluble

sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Suitable enzyme stabilizers and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115 and 5,576,282.

Disrupting Agents

5 As it was stated above, the detergent tablet of the present invention may further comprise a disrupting agent. Disrupting agents are typically included in the tablet at levels of from about 5% to about 60%, and more preferably from about 20% to about 50%, by weight. The disrupting agent may be a disintegrating or effervescing agent. Suitable disintegrating agents include agents that swell on contact with water or facilitated water influx and/or efflux by forming channels in
10 compressed and/or non-compressed portions. Any known disintegrating or effervescing agent suitable for use in laundry or dishwashing applications is envisaged for use herein. Suitable disintegrating agent include starch, starch derivatives, alginates, carboxymethylcellulose (CMC), cellulosic-based polymers, sodium acetate, aluminium oxide. Suitable effervescing agents are those that produce a gas on contact with water. Suitable effervescing agents may be oxygen,
15 nitrogen dioxide or carbon dioxide evolving species. Examples of preferred effervescing agents may be selected from the group consisting of perborate, percarbonate, carbonate, bicarbonate and carboxylic acids such as citric or maleic acid.

Builders - When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about
20 50%, more preferably to about 30% by weight, of detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Preferred builders for use in the detergent and cleaning compositions, particularly dishwashing compositions, especially automatic dishwashing compositions or detergents ("ADD" or "ADW") described herein include, but are not limited to, water-soluble builder
25 compounds, (for example polycarboxylates) as described in U.S. Patent Nos. 5,695,679, 5,705,464 and 5,710,115. Other suitable polycarboxylates are disclosed in U.S. Patent Nos. 4,144,226, 3,308,067 and 3,723,322. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly titrates.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali
30 metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates (see, for example, U.S. Patent Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137), phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

35 However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak"

builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Preferably, the silicates are water-soluble silicates, more preferably they are any silicates which are soluble to the extent that they do not adversely affect spotting/filming characteristics of the ADD composition.

Suitable silicates include the water-soluble sodium silicates with an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from about 1.0 to 2.8, with ratios of from about 1.6 to 2.4 being preferred, and about 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0 is the most preferred. Silicates, when present, are preferably present in the detergent and cleaning compositions described herein at a level of from about 5% to about 50% by weight of the composition, more preferably from about 10% to about 40% by weight.

Partially soluble or insoluble builder compounds, which are suitable for use in the detergent and cleaning compositions, particularly granular detergent compositions, include, but are not limited to, crystalline layered silicates, preferably crystalline layered sodium silicates (partially water-soluble) as described in U.S. Patent No. 4,664,839, and sodium aluminosilicates (water-insoluble). When present in detergent and cleaning compositions, these builders are typically present at a level of from about 1% to 80% by weight, preferably from about 10% to 70% by weight, most preferably from about 20% to 60% by weight of the composition.

Crystalline layered sodium silicates having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from about 1.9 to about 4, preferably from about 2 to about 4, most preferably 2, and y is a number from about 0 to about 20, preferably 0 can be used in the compositions described herein. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. The most preferred material is delta- Na_2SiO_5 , available from Hoechst AG as NaSKS-6 (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. SKS-6 is a highly preferred layered silicate for use in the compositions described herein herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used in the compositions described herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates particularly useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRITESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionizable material. The solid, water-soluble ionizable material is preferably selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Also suitable in the detergent compositions described herein are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

Dispersants - One or more suitable polyalkyleneimine dispersants may be incorporated into the cleaning compositions of the present invention. Examples of such suitable dispersants can be found in European Patent Application Nos. 111,965, 111,984, and 112,592; U.S. Patent Nos. 4,597,898, 4,548,744, and 5,565,145. However, any suitable clay/soil dispersant or anti-redeposition agent can be used in the laundry compositions of the present invention.

In addition, polymeric dispersing agents which include polymeric polycarboxylates and polyethylene glycols, are suitable for use in the present invention. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid

polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in U.S. 3,308,067.

5 Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1
10 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful
15 dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition
20 agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a
25 molecular weight (avg.) of about 10,000.

Chelating Agents - The compositions of the present invention herein may also optionally contain a chelating agent which serves to chelate metal ions and metal impurities which would otherwise tend to deactivate the bleaching agent(s). Useful chelating agents can include amino
30 carboxylates, phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Further examples of suitable chelating agents and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115, 5,728,671 and 5,576,282.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble
builders such as zeolites, layered silicates and the like.

35 If utilized, these chelating agents will generally comprise from about 0.1% to about 15%, more preferably from about 0.1% to about 3.0% by weight of the detergent compositions herein.

Corrosion inhibitor compound - The detergent tablets of the present invention suitable for use in dishwashing methods may contain corrosion-inhibitors preferably selected from organic silver coating agents, particularly paraffin, nitrogen-containing corrosion inhibitor compounds and Mn(II) compounds, particularly Mn(II) salts of organic ligands.

5 Organic silver coating agents are described in PCT Publication No. WO94/16047 and copending European application No. EP-A-690122. Nitrogen-containing corrosion inhibitor compounds are disclosed in copending European Application no. EP-A-634,478. Mn(II) compounds for use in corrosion inhibition are described in copending European Application No. EP-A-672 749.

10 Organic silver coating agent, when present, may be incorporated at a level of preferably from about 0.05% to about 10%, more preferably from about 0.1% to about 5% by weight of the total composition.

15 The functional role of the silver coating agent is to form 'in use' a protective coating layer on any silverware components of the washload to which the compositions of the invention are being applied. The silver coating agent should hence have a high affinity for attachment to solid silver surfaces, particularly when present in as a component of an aqueous washing and bleaching solution with which the solid silver surfaces are being treated.

20 Suitable organic silver coating agents herein include, but are not limited to, fatty esters of mono- or polyhydric alcohols having from about 1 to about 40 carbon atoms in the hydrocarbon chain.

25 The fatty acid portion of the fatty ester can be obtained from mono- or poly-carboxylic acids having from about 1 to about 40 carbon atoms in the hydrocarbon chain. Suitable examples of monocarboxylic fatty acids include behenic acid, stearic acid, oleic acid, palmitic acid, myristic acid, lauric acid, acetic acid, propionic acid, butyric acid, isobutyric acid, Valeric acid, lactic acid, glycolic acid and β,β' -dihydroxyisobutyric acid. Examples of suitable polycarboxylic acids include: n-butyl-malonic acid, isocitric acid, citric acid, maleic acid, malic acid and succinic acid.

30 The fatty alcohol radical in the fatty ester can be represented by mono- or polyhydric alcohols having from about 1 to about 40 carbon atoms in the hydrocarbon chain. Examples of suitable fatty alcohols include; behenyl, arachidyl, cocoyl, oleyl and lauryl alcohol, ethylene glycol, glycerol, ethanol, isopropanol, vinyl alcohol, diglycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan.

Preferably, the fatty acid and/or fatty alcohol group of the fatty ester adjunct material have from about 1 to about 24 carbon atoms in the alkyl chain.

Preferred fatty esters herein are ethylene glycol, glycerol and sorbitan esters wherein the fatty acid portion of the ester normally comprises a species selected from behenic acid, stearic acid, oleic acid, palmitic acid or myristic acid.

5 The glycerol esters are also highly preferred. These are the mono-, di- or tri-esters of glycerol and the fatty acids as defined above.

Specific examples of fatty alcohol esters for use herein include: stearyl acetate, palmityl di-lactate, cocoyl isobutyrate, oleyl maleate, oleyl dimaleate, and tallowyl propionate. Some fatty acid esters useful herein include: xylitol monopalmitate, pentaerythritol monostearate, sucrose monostearate, glycerol monostearate, ethylene glycol monostearate, sorbitan esters.

10 Suitable sorbitan esters include sorbitan monostearate, sorbitan palmitate, sorbitan monolaurate, sorbitan monomyristate, sorbitan monobehenate, sorbitan mono-oleate, sorbitan dilaurate, sorbitan distearate, sorbitan dibehenate, sorbitan dioleate, and also mixed tallowalkyl sorbitan mono- and di-esters.

Glycerol monostearate, glycerol mono-oleate, glycerol monopalmitate, glycerol monobehenate, and glycerol distearate are preferred glycerol esters herein.

15

Suitable organic silver coating agents include triglycerides, mono or diglycerides, and wholly or partially hydrogenated derivatives thereof, and any mixtures thereof. Suitable sources of fatty acid esters include vegetable and fish oils and animal fats. Suitable vegetable oils include soy bean oil, cotton seed oil, castor oil, olive oil, peanut oil, safflower oil, sunflower oil, rapeseed oil, grapeseed oil, palm oil and corn oil.

20

Waxes, including microcrystalline waxes are suitable organic silver coating agents herein. Preferred waxes have a melting point in the range from about 35°C to about 110°C and comprise generally from about 12 to about 70 carbon atoms. Preferred are petroleum waxes of the paraffin and microcrystalline type which are composed of long-chain saturated hydrocarbon compounds.

25

Alginates and gelatin are suitable organic silver coating agents which can be used in the compositions herein.

Dialkyl amine oxides such as about C₁₂ to about C₂₀ methylamine oxide, and dialkyl quaternary ammonium compounds and salts, such as the about C₁₂ to about C₂₀ methylammonium halides are also suitable.

30

Other suitable organic silver coating agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from about 12,000 to about 700,000, polyethylene glycols (PEG) with an average molecular weight of from about 600 to about 10,000, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, and cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose are examples of such polymeric materials.

35

Certain perfume materials, particularly those demonstrating a high substantivity for metallic surfaces, are also useful as the organic silver coating agents herein.

Polymeric soil release agents can also be used as an organic silver coating agent.

A preferred organic silver coating agent is a paraffin oil, typically a predominantly
5 branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil selected from predominantly branched C₂₅₋₄₅ species with a ratio of cyclic to noncyclic hydrocarbons of from about 1:10 to about 2:1, preferably from about 1:5 to about 1:1. A paraffin oil meeting these characteristics, having a ratio of cyclic to noncyclic hydrocarbons of about 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name
10 WINOG 70.

Suitable nitrogen-containing corrosion inhibitor compounds include imidazole and derivatives thereof such as benzimidazole, 2-heptadecyl imidazole and those imidazole derivatives described in Czech Patent No. 139, 279 and British Patent GB-A-1,137,741, which also discloses a method for making imidazole compounds.

15 Also suitable as nitrogen-containing corrosion inhibitor compounds are pyrazole compounds and their derivatives, particularly those where the pyrazole is substituted in any of the 1, 3, 4 or 5 positions by substituents R₁, R₃, R₄ and R₅ where R₁ is any of H, CH₂OH, CONH₃, or COCH₃, R₃ and R₅ are any of C₁-C₂₀ alkyl or hydroxyl, and R₄ is any of H, NH₂ or NO₂.

Other suitable nitrogen-containing corrosion inhibitor compounds include benzotriazole,
20 2-mercaptobenzothiazole, 1-phenyl-5-mercapto-1,2,3,4-tetrazole, thionalide, morpholine, melamine, distearylamine, stearoyl stearamide, cyanuric acid, aminotriazole, aminotetrazole and indazole.

Nitrogen-containing compounds such as amines, especially distearylamine and ammonium compounds such as ammonium chloride, ammonium bromide, ammonium sulphate or
25 diammonium hydrogen citrate are also suitable.

The detergent tablets may contain an Mn(II) corrosion inhibitor compound. The Mn(II) compound is preferably incorporated at a level of from about 0.005% to about 5% by weight, more preferably from about 0.01% to about 1%, most preferably from about 0.02% to about 0.4% by weight of the compositions. Preferably, the Mn(II) compound is incorporated at a level to
30 provide from about 0.1 ppm to about 250 ppm, more preferably from about 0.5 ppm to about 50 ppm, even more preferably from about 1 ppm to about 20 ppm by weight of Mn(II) ions in any bleaching solution.

The Mn (II) compound may be an inorganic salt in anhydrous, or any hydrated forms. Suitable salts include manganese sulphate, manganese carbonate, manganese phosphate,
35 manganese nitrate, manganese acetate and manganese chloride. The Mn(II) compound may be a salt or complex of an organic fatty acid such as manganese acetate or manganese stearate.

The Mn(II) compound may be a salt or complex of an organic ligand. In one preferred aspect the organic ligand is a heavy metal ion sequestrant. In another preferred aspect the organic ligand is a crystal growth inhibitor.

Other suitable additional corrosion inhibitor compounds include, mercaptans and diols, especially mercaptans with about 4 to about 20 carbon atoms including lauryl mercaptan, thiophenol, thionaphthol, thionalide and thioanthranol. Also suitable are saturated or unsaturated C₁₀-C₂₀ fatty acids, or their salts, especially aluminium tristearate. The C₁₂-C₂₀ hydroxy fatty acids, or their salts, are also suitable. Phosphonated octa-decane and other anti-oxidants such as beta-hydroxytoluene (BHT) are also suitable.

Copolymers of butadiene and maleic acid, particularly those supplied under the trade reference no. 07787 by Polysciences Inc. have been found to be of particular utility as corrosion inhibitor compounds.

Another preferred detergent active component for use in the present invention is a hydrocarbon oil, typically a predominantly long chain, aliphatic hydrocarbons having a number of carbon atoms in the range of from about 20 to about 50; preferred hydrocarbons are saturated and/or branched; preferred hydrocarbon oil selected from predominantly branched C₂₅₋₄₅ species with a ratio of cyclic to noncyclic hydrocarbons of from about 1:10 to about 2:1, preferably from about 1:5 to about 1:1. A preferred hydrocarbon oil is paraffin. A paraffin oil meeting the characteristics as outlined above, having a ratio of cyclic to noncyclic hydrocarbons of about 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

The detergent tablets of the present invention suitable for use in dishwashing methods may contain a water-soluble bismuth compound, preferably present at a level of from about 0.005% to about 20%, more preferably from about 0.01% to about 5%, even more preferably from about 0.1% to about 1% by weight of the compositions.

The water-soluble bismuth compound may be essentially any salt or complex of bismuth with essentially any inorganic or organic counter anion. Preferred inorganic bismuth salts are selected from the bismuth trihalides, bismuth nitrate and bismuth phosphate. Bismuth acetate and citrate are preferred salts with an organic counter anion.

Colorant - The term 'colorant', as used herein, means any substance that absorbs specific wavelengths of light from the visible light spectrum. Such colorants when added to a detergent composition have the effect of changing the visible color and thus the appearance of the detergent composition. Colorants may be for example either dyes or pigments. Preferably the colorants are stable in composition in which they are to be incorporated. Thus in a composition of high pH the colorant is preferably alkali stable and in a composition of low pH the colorant is preferably acid stable.

The compressed and/or non-compressed, non-encapsulating portions may contain a colorant, a mixture of colorants, colored particles or mixture of colored particles such that the compressed portion and the non-compressed, non-encapsulating portion have different visual appearances. Preferably one of either the compressed portion or the non-compressed, non-encapsulating portion a colorant. The compressed and/or non-compressed, non-encapsulating portions may also be of one color and contain particles or speckles, of another color. For example the compressed portion could be white with blue speckles, while the non-compressed, non-encapsulating portion is blue.

Where the non-compressed, non-encapsulating portion comprises two or more compositions of detergent active components, preferably at least one of either the first and second and/or subsequent compositions comprises a colorant. Where both the first and second and/or subsequent compositions comprise a colorant it is preferred that the colorants have a different visual appearance.

Where present the coating layer preferably comprises a colorant. Where the compressed portion and the coating layer comprise a colorant, it is preferred that the colorants provide a different visual effect.

Examples of suitable dyes include reactive dyes, direct dyes, azo dyes. Preferred dyes include phthalocyanine dyes, anthraquinone dye, quinoline dyes, monoazo, disazo and polyazo. More preferred dyes include anthraquinone, quinoline and monoazo dyes. Preferred dyes include SANDOLAN E-HRL 180% (tradename), SANDOLAN MILLING BLUE (tradename), TURQUOISE ACID BLUE (tradename) and SANDOLAN BRILLIANT GREEN (tradename) all available from Clariant UK, HEXACOL QUINOLINE YELLOW (tradename) and HEXACOL BRILLIANT BLUE (tradename) both available from Pointings, UK, ULTRA MARINE BLUE (tradename) available from Holliday or LEVAFIX TURQUOISE BLUE EBA (tradename) available from Bayer, USA.

Furthermore, it is preferred that the colorant does not cause visible staining to plastic, such as an automatic dishwasher or plastic tableware, after a plurality of cycles, more preferably between 1 and 50 cycles.

The colorant may be incorporated into the compressed and/or non-compressed, non-encapsulating portion by any suitable method. Suitable methods include mixing all or selected detergent active components with a colorant in a drum or spraying all or selected detergent active components with the colorant in a rotating drum. Alternatively, the colorants color may be improved by predissolving the colorant in a compatible solvent prior to addition of the colorant to the composition.

Colorant when present as a component of the compressed portion is present at a level of from about 0.001% to about 1.5%, preferably from about 0.01% to about 1.0%, most preferably

from about 0.1% to about 0.3%. When present as a component of the non-compressed, non-encapsulating portion, colorant is generally present at a level of from about 0.001% to about 0.1%, more preferably from about 0.005% to about 0.05%, most preferably from about 0.007% to about 0.02%. When present as a component of the coating layer, colorant is present at a level of from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.1%, most preferably from about 0.03% to about 0.06%.

Silicone and Phosphate Ester Suds Suppressors - The compositions of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Preferably, the suds suppressors, when present, are silicone and/or silica-silicone mixtures, as disclosed in U.S. Patent Nos. 5,707,950 and 5,728,671. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%, more preferably from about 0.001% to 2%, most preferably from about 0.01% to 1% by weight of the cleaning composition. However, generally (for cost considerations and/or deposition) preferred compositions herein do not comprise suds suppressors or comprise suds suppressors only at low levels, e.g., less than about 0.1% of active suds suppressing agent.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

If it is desired to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate

esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

pH and Buffering Variation

The detergent compositions herein can be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

The preferred compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the composition is dissolved in water at a concentration of 1,000 - 10,000 ppm, the pH remains in the range of above about 8, preferably from about 9.5 to about 11. The preferred nonphosphate pH-adjusting component of the invention is selected from the group consisting of:

- (i) sodium carbonate or sesquicarbonate;
- (ii) sodium silicate, preferably hydrous sodium silicate having $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantities of sodium metasilicate;
- (iii) sodium citrate;
- (iv) citric acid;
- (v) sodium bicarbonate;
- (vi) sodium borate, preferably borax;
- (vii) sodium hydroxide; and
- (viii) mixtures of (i)-(vii).

Preferred embodiments contain low levels of silicate (i.e. from about 3% to about 10% SiO_2).

The amount of the pH adjusting component in the instant composition is preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the composition in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

The preferred ADD compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders as described in U.S. Patent Nos. 5,705,464 and 5,710,115.

Material Care Agents - The preferred ADD compositions may contain one or more material care agents which are effective as anti-tarnish aids as described in U.S. Patent Nos. 5,705,464, 5,710,115 and 5,646,101.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the ADD composition.

Other Materials - Deterasive ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as dyes, fillers, germicides, alkalinity sources, hydrotropes, anti-oxidants, perfumes, solubilizing agents, carriers, processing aids, and pigments as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101.

Tablet Form

As mentioned above, the composition of the present invention can be in a tablet form, especially a dimple tablet, which is preferred for use in automatic dishwashing machines.

A preferred dimple tablet of the composition of the present invention and means for producing such a dimple tablet follows.

The preferred dimple tablet comprises (A) at least one compressed solid body portion (the tablet body) and (B) at least one non-compressed, non-encapsulating portion (the dimple portion). The use of the non-compressed, non-encapsulating portion(s) and compressed portion(s) provides a superior delivery mechanism for detergent active agents into the domestic wash process. Either of the non-compressed, non-encapsulating portion(s) or the compressed portion(s) can rapidly dissolve or disperse thereby providing for the earliest possible delivery of detergent active agents into the domestic wash process.

The detergent tablet must have a ratio of B to A from about 1:50 to about 4:1, preferably from about 1:20 to about 1:1, more preferably about 1:10 to about 1:1, by area. Area A is the area of the detergent tablet, but excluding the area of the mould. Area B is the area of the non-compressed, non-encapsulating portion/s.

The ratio of B to A gives optimal dissolution kinetics to the dimple. Additionally, the non-compressed, non-encapsulating portion/s have improved visual noticibility.

The detergent tablet, the mould(s) and non-compressed, non-encapsulating portion(s) can be of any conceivable size and shape as long as the ratio of B to A remains from about 1:50 to about 4:1. Preferably, when the detergent tablet is to be used in a dispensing device, such as those found in automatic dishwashers, the detergent tablet will be of a size suitable to be dispensed from the dispenser.

Accordingly, by using this preferred dimple tablet, the detergent active components of a detergent tablet previously adversely affected by the compression pressure used to form the tablets may now be included in a detergent tablet. Examples of these components include bleaching agents and enzymes, such as the endolase enzyme of the present invention. In addition, these detergent active components may be separated from one another by having one or more compatible components contained in the compressed portion and one or more compatible components contained in the non-compressed, non-encapsulating portion(s) of the tablet. Examples of components that may interact and may therefore require separation include bleaching agents, bleach activators or catalyst and enzymes; bleaching agents and bleach catalysts or activators; bleaching agents and surfactants; alkalinity sources and enzymes.

It may be advantageous to provide the compressed and the non-compressed, non-encapsulating portion(s) such that they dissolve in the wash water with different dissolution rates. By controlling the rate of dissolution of each portion relative to one another, and by selection of the detergent active components in the respective portions, their order of release into the wash water can be controlled and the cleaning performance of the detergent tablet may be improved. For example it is often preferred that enzymes are delivered to the wash prior to bleaching agent and/or bleach activator. It may also be preferred that a source of alkalinity is released into the wash water more rapidly than other components of the detergent tablet. It is also envisaged that it may be advantageous to prepare a detergent tablet according to the present invention wherein the release of certain components of the tablet is delayed relative to other components.

The tablet may also comprise a plurality of moulds in the compressed solid body portion. These plurality of moulds may be overlapping or be distinctly separate.

The tablet may also comprise a plurality non-compressed, non-encapsulating portions. Such a plurality of non-compressed, non-encapsulating portions may be advantageous, enabling a tablet to be produced which has for example, a first and second and optional subsequent portions so that they have different rates of dissolution. Such performance benefits are achieved by selectively delivering detergent active components into the wash water at different times.

It is preferred that the detergent tablets, of the present invention be free from foul or noxious odors. If present such odors may be masked or removed. This includes the addition of masking agents, perfumes, odor absorbers, such as cyclodextrins, etc.

The detergent tablet can be transparent, opaque or any possible shade in between these two extremes. The compressed solid body and the at least one non-compressed, non-encapsulating portion can have the same or different degree of transparency, i.e. ranging from totally transparent to opaque. However, it is preferred that they be different. When there are more than one non-compressed, non-encapsulating portion present in the detergent tablet it is possible for each of the non-compressed, non-encapsulating portion to have the same or different

degree of transparency, i.e. ranging from totally transparent to opaque. However, it is preferred that they be different.

Furthermore, it is preferred that greater than 90%, more preferably 95%, even more preferably 98%, of the at least one non-compressed, non-encapsulating portion be free from visible cracks after one week of storage at ambient conditions. Additionally, it is preferred that any gaps between the compressed solid body and the at least one non-compressed, non-encapsulating portion be less than 1 mm, more preferably 0.75 mm, even more preferably 0.5 mm, after one week of storage at ambient conditions.

The detergent tablets described herein are preferably between 15g and 100g in weight, more preferably between 18g and 80g in weight, even more preferably between 20g and 60g in weight. The detergent tablet described herein that are suitable for use in automatic dishwashing methods are most preferably between 20g and 40g in weight. Detergent tablets suitable for use in fabric laundering methods are most preferably between 40g and 100g, more preferably between 40g and 80g, most preferably between 40g and 65g in weight. The weight ratio of compressed portion to non-compressed, gel portion is generally greater than 0.5:1, preferably greater than 1:1, more preferably greater than 2:1, even more preferably greater than 3:1 or even 4:1, most preferably at least 5:1.

The compressed portions of the detergent tablets described herein have Child Bite Strength (CBS) which is generally greater than 10Kg, preferably greater than 12Kg, most preferably greater than 14Kg. CBS is measured as per the U.S. Consumer Product Safety Commission Test Specification.

The dissolution rate of the at least one non-compressed, non-encapsulating portion can be greater than the dissolution rate of the compressed portion determined using the SOTAX dissolution test method. Alternatively, the dissolution rate of the compressed portion can be greater than the dissolution rate of the at least one non-compressed, non-encapsulating portion determined using the SOTAX dissolution test method.

Dissolution rate is measured using the SOTAX dissolution test method. For the purposes of the present invention dissolution of detergent tablets is achieved using a SOTAX (tradename) machine; model number AT7 available from SOTAX.

SOTAX Dissolution Test Method: The SOTAX machine consists of a temperature controlled waterbath with lid. 7 pots are suspended in the water bath. 7 electric stirring rods are suspended from the underside of the lid, in positions corresponding to the position of the pots in the waterbath. The lid of the waterbath also serves as a lid on the pots.

The SOTAX waterbath is filled with water and the temperature gauge set to 50°C. Each pot is then filled with 1 litre of deionised water and the stirrer set to revolve at 250rpm. The lid

of the waterbath is closed, allowing the temperature of the deionised water in the pots to equilibrate with the water in the waterbath for 1 hour.

The compressed portion and non-compressed, non-encapsulating portion(s) are weighed and one tablet is placed in each pot, the lid is then closed. The compressed portion and non-compressed, non-encapsulating portion/s is visually monitored until it completely dissolves. The time is noted when the compressed portion and non-compressed, non-encapsulating portion(s) has completely dissolved. The dissolution rate of the compressed portion and non-compressed, non-encapsulating portion(s) is calculated as the average weight (g) of tablet dissolved in deionized water per minute.

10 a. Compressed portion

The compressed portion of the detergent tablet comprises at least one detergent active component described herein but may comprise a mixture of more than one detergent active components, which are compressed. Any detergent tablet component conventionally used in known detergent tablets is suitable for incorporation into the compressed portion of the detergent tablets of this invention.

Detergent active component(s) present in the compressed layer may optionally be prepared in combination with a carrier and/or a binder for example polymer (e.g. PEG), liquid silicate. The detergent active components are preferably prepared in particulate form (i.e. powder or granular form) and may be prepared by any known method, for example conventional spray drying, granulation or agglomeration. The particulate detergent active component(s) are then compressed using any suitable equipment suitable for forming compressed tablets, blocks, bricks or briquettes; described in more detail hereafter.

The compressed solid body portion preferably has at least one mould on a surface of the compressed solid body portion. The non-compressed, non-encapsulating portion(s) are mounted in to the moulds.

The compressed solid body portion may also be provided with a coating of a water-soluble material to protect the body portion. The coating layer preferably comprises a material that becomes solid on contacting the compressed and/or the non-compressed portions within preferably less than 15 minutes, more preferably less than 10 minutes, even more preferably less than 5 minutes, most preferably less than 60 seconds. Preferably the coating layer is water-soluble. Preferred coating layers comprise materials selected from the group consisting of fatty acids, alcohols, diols, esters and ethers, adipic acid, carboxylic acid, dicarboxylic acid, polyvinyl acetate (PVA), polyvinyl pyrrolidone (PVP), polyacetic acid, polyethylene glycol (PEG) and mixtures thereof. Preferred carboxylic or dicarboxylic acids preferably comprise an even number of carbon atoms. Preferably carboxylic or dicarboxylic acids comprise at least 4, more preferably at least 6, even more preferably at least 8 carbon atoms, most preferably between 8 and 13 carbon

atoms. Preferred dicarboxylic acids include adipic acid, suberic acid, azelaic acid, subacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. Preferred fatty acids are those having a carbon chain length of from C12 to C22, most preferably from C18 to C22. The coating layer may also preferably comprise a disrupting agent. Where present the coating layer generally present at a level of at least 0.05%, preferably at least 0.1%, more preferably at least 1%, most preferably at least 2% or even at least 5% of the detergent tablet. However, when the detergent tablet is an automatic dishwashing composition, it is preferred that when the compressed portion is coated that the coating not be a fatty acid.

b. Non-Compressed, Non-Encapsulating Portion

The non-compressed, non-encapsulating portion comprises detergent active components, preferably the multi-function component of the present invention, and optionally, comprises other detergent active components, preferably other enzymes, more preferably an amylase.

The detergent active component(s) may be in any form for example particulate (i.e. powder or granular), gel or liquid form. The non-compressed, non-encapsulating portion in addition to comprising an detergent active component, may also optionally comprise a carrier component. The detergent active component may be present in the form of a solid, gel or liquid, prior to combination with a carrier component.

The non-compressed, non-encapsulating portion is formulated such that the detergent active ingredient is essentially completely delivered in a short period of time. Typically, the gel portion is formulated so that at least about 80% of the detergent active is delivered to the wash of a domestic washing process within the first 5 minutes, more preferably at least about 90% in the first 3 minutes and even more preferably 95% within the first 2 minutes.

The non-compressed, non-encapsulating portion of the detergent tablet may be in solid, gel, liquid or powder form.

The detergent tablet of the present invention requires that the non-compressed, non-encapsulating portion be delivered to the compressed portion such that the compressed portion and non-compressed, non-encapsulating portion contact each other. The non-compressed, non-encapsulating portion may be delivered to the compressed portion in solid or flowable form.

Where the non-compressed, non-encapsulating portion is in solid form, it is pre-prepared, optionally shaped and then delivered to the compressed portion. The non-compressed, non-encapsulating portion is then affixed to a pre-formed compressed portion, for example by adhesion or by insertion of the non-compressed, non-encapsulating portion to a co-operating surface of the compressed portion. The compressed portion comprises at least one mould into which the non-compressed, non-encapsulating portion/s is/are delivered.

The non-compressed, non-encapsulating portion is preferably delivered to the compressed portion in flowable form. The non-compressed, non-encapsulating portion is then affixed to the compressed portion for example by adhesion, by forming a coating over the non-compressed, non-encapsulating layer to secure it to the compressed portion, or by hardening, for example (i) by cooling to below the melting point where the flowable composition becomes a solidified melt; (ii) by evaporation of a solvent; (iii) by crystallization; (iv) by polymerization of a polymeric component of the flowable non-compressed, non-encapsulating portion; (v) through pseudo-plastic properties where the flowable non-compressed, non-encapsulating portion comprises a polymer and shear forces are applied to the non-compressed, non-encapsulating portion; (vi) combining a binding agent with the flowable non-compressed, non-encapsulating portion. In an alternative embodiment the flowable non-compressed, non-encapsulating portion may be an extrudate that is affixed to the compressed portion by for example any of the mechanism described above or by expansion of the extrudate to the parameters of a mould provided by the compressed portion.

The compressed portion comprises at least one mould into which the non-compressed non-encapsulated portion(s) is/are delivered. In an alternative embodiment the surface of the compressed portion comprises more than one mould into which the non-compressed, non-encapsulating portion may be delivered. The mould(s) preferably at least partially accommodates one or more non-compressed, non-encapsulating portions. The non-compressed, non-encapsulating portion(s) is then delivered into the mould(s) and affixed to the compressed portion as described above. Alternatively, the detergent tablet contains one mould in which there are two non-compressed, non-encapsulating portions. The first non-compressed, non-encapsulating portion could be added as a liquid, which is allowed to set or harden, or as a pre formed gel. These two different non-compressed, non-encapsulating portion could have different rates of dissolution.

The non-compressed, non-encapsulating portion may comprise particulates, such as powders or granules. The particulates may be prepared by any known method, for example conventional spray drying, granulation, encapsulation or agglomeration. Particulates may be affixed to the compressed portion by incorporating a binding agent or by forming a coating layer over the non-compressed, non-encapsulating portion.

Where the detergent tablet comprises more than one non-compressed, non-encapsulating portion, the first and second and optional subsequent non-compressed, non-encapsulating portion may comprise particulates having substantially different average particle size. By substantially different average particle size we mean that the difference between the average particle size of the first and second and/or subsequent compositions is greater than 5%, preferably greater than 10%, more preferably greater than 15% or even 20% of the smaller average particle size.

The average particle size of the particulate detergent active components used herein is calculated using a series of Tyler sieves. The series consists of a number of sieves each having a different aperture size. Samples of a composition of detergent active components are sieved through the series of sieves (typically 5 sieves). The weight of a sample of composition retained in the sieve is plotted against the aperture size of the sieve. The average particle size of the composition is defined as the aperture size through which 50% by weight of the sample of composition would pass.

Alternatively, compositions containing more than one detergent active components can have substantially different density. For example, the difference between the density of the first and second and/or subsequent compositions can be greater than about 5%, more preferably greater than about 10%, even more preferably greater than about 15% or even about 20% of the smaller density. Density of the particulate composition of detergent active components can be measured by any known method suitable for measuring density of particulate material.

Preferably, the density of the composition of detergent active components is measured using a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

A density measurement is taken by hand pouring the composition into the funnel. Once the funnel is filled, the flap valve is opened and powder allowed to run through the funnel, overfilling the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in grams/litre. Replicate measurements are made as required.

Tablets in which one or more of the non-compressed, non-encapsulating portion comprise particulates and the average particle size and/or density of the first and the subsequent non-compressed, non-encapsulating portions are substantially different are preferred where the first and second and optionally subsequent non-compressed, non-encapsulating portions are required to have different rates of dissolution.

Where the non-compressed, non-encapsulating portion comprises a solidified melt, the melt is prepared by heating a composition comprising a detergent active component and optional carrier component(s) to above its melting point to form a flowable melt. The flowable melt is then poured into a mould in the surface of the compressed portion and allowed to cool. As the

melt cools it becomes solid, taking the shape of the mould at ambient temperature. Where the composition comprises one or more carrier components, the carrier component(s) may be heated to above their melting point, and then a detergent active component may be added. Carrier components suitable for preparing a solidified melt are typically non-active components that can be heated to above melting point to form a liquid and cooled to form an intermolecular matrix that can effectively trap detergent active components. A preferred non-active carrier component is an organic polymer that is solid at ambient temperature. Preferably the non-active detergent component is polyethylene glycol (PEG). The compressed portion of the detergent tablet provides at least one mould to accommodate the melt.

10 The flowable non-compressed, non-encapsulating portion may be in a form comprising a dissolved or suspended detergent active component. The flowable non-compressed, non-encapsulating portion may harden over time to form a solid, semi-solid or highly viscous liquid non-compressed, non-encapsulating portion by any of the methods described above. In particular, the flowable non-compressed, non-encapsulating portion may harden by evaporation of a solvent. Solvents suitable for use herein may include any known solvent in which a binding agent is soluble. Preferred solvents may be polar or non-polar and may include water, alcohol, (for example ethanol, acetone) and alcohol derivatives. In an alternative embodiment more than one solvent may be used.

20 The flowable non-compressed, non-encapsulating portion may comprise one or more binding agents. Any binding agent that has the effect of causing the composition to become solid, semi-solid or highly viscous over time is envisaged for use herein. Although not wishing to be bound by theory, it is believed that mechanisms by which the binding agent causes a non-solid composition to become solid, semi-solid or highly viscous include: chemical reaction (such as chemical cross linking), or interaction between two or more components of the flowable compositions either; chemical or physical interaction of the binding agent with a component of the composition. Preferred binding agents include a sugar/gelatine combination, starch, glycerol and organic polymers. The sugar may be any monosaccharide (e.g. glucose), disaccharide (e.g. sucrose or maltose) or polysaccharide. The most preferred sugar is commonly available sucrose. For the purposes of the present invention type A or B gelatine may be used, available from for example Sigma. Type A gelatine is preferred since it has greater stability in alkaline conditions in comparison to type B. Preferred gelatine also has a bloom strength of between 65 and 300, most preferably between 75 and 100. Preferred organic polymers include polyethylene glycol (PEG) of molecular weight from 500 to 10,000, preferably from 750 to 8000, most preferably from 1000 to 6000 available from for example from Hoechst.

35 Where the non-compressed, non-encapsulating portion is an extrudate, the extrudate is prepared by premixing the detergent active components with optional carrier components to form

a viscous paste. The viscous paste is then extruded using any suitable commonly available extrusion equipment such as for example a single or twin screw extruder available from for—
example APV Baker, Peterborough, U.K. The extrudate is then cut to size either after delivery to the compressed portion, or prior to delivery to the compressed portion of the detergent tablet.

- 5 The compressed portion of the tablet comprises at least one mould into which the extruded non-compressed, non-encapsulating portion is delivered.

In a preferred embodiment the non-compressed, non-encapsulating portion is coated with a coating layer. The coating may be used to affix a non-compressed, non-encapsulating portion to the compressed portion. This may be particularly advantageous where the non-compressed,
10 non-encapsulating portion comprises flowable particulates, gels or liquids.

The coating layer preferably comprises a material that becomes solid on contacting the compressed and/or the non-compressed, non-encapsulating portions within preferably less than 15 minutes, more preferably less than 10 minutes, even more preferably less than 5 minutes, most preferably less than 60 seconds. Preferably the coating layer is water-soluble. Preferred coating
15 layers comprise materials selected from the group consisting of fatty acids, alcohols, diols, esters and ethers, adipic acid, carboxylic acid, dicarboxylic acid, polyvinyl acetate (PVA), polyvinyl pyrrolidone (PVP), polyacetic acid, polyethylene glycol (PEG) and mixtures thereof. Preferred carboxylic or dicarboxylic acids preferably comprise an even number of carbon atoms. Preferably carboxylic or dicarboxylic acids comprise at least 4, more preferably at least 6, even more
20 preferably at least 8 carbon atoms, most preferably between 8 and 13 carbon atoms. Preferred dicarboxylic acids include adipic acid, suberic acid, azelaic acid, subacic acid, undecanedioic acid, dodecandioic acid, tridecanedioic and mixtures thereof. Preferred fatty acids are those having a carbon chain length of from C12 to C22, most preferably from C18 to C22. The coating layer may also preferably comprise a disrupting agent. Where present the coating layer generally
25 present at a level of preferably at least about 0.05%, more preferably at least about 0.1%, even more preferably at least about 1%, even more preferably still at least about 2% or even at least about 5% of the detergent tablet. However, when the detergent tablet is an automatic dishwashing composition, it is preferred that the coating not be a fatty acid.

As an alternative embodiment the coating layer may encapsulate the detergent tablet. In
30 this embodiment the coating layer is present at a level of at least about 4%, more preferably at least about 5%, most preferably at least about 10% of the detergent tablet.

In a preferred embodiment the compressed and/or non-compressed, non-encapsulating portions and/or coating layer additionally comprise a disrupting agent. The disrupting agent may be a disintegrating or effervescent agent. Suitable disintegrating agents include agents that swell
35 on contact with water or facilitated water influx and/or efflux by forming channels in compressed and/or non-compressed, non-encapsulating portions. Any known disintegrating or effervescent

agent suitable for use in laundry or dishwashing applications is envisaged for use herein.

Suitable disintegrating agent include starch, starch derivatives, alginates, carboxymethylcellulose (CMC); cellulosic-based polymers; sodium acetate; aluminium oxide. -Suitable effervescing agents are those that produce a gas on contact with water. Suitable effervescing agents may be oxygen, nitrogen dioxide or carbon dioxide evolving species. Examples of preferred effervescing agents may be selected from the group consisting of perborate, percarbonate, carbonate, bicarbonate and carboxylic acids such as citric or maleic acid.

An advantage of including a disrupting agent in the detergent tablet of the present invention is the transport, storage and handling benefits that can be achieved by increasing the hardness of the detergent tablet without adversely affecting the cleaning performance.

The non-compressed, non-encapsulating portion may additionally contain a drying agent. Any, conventional drying agent can be used. See Vogel's Text book of Practical Organic Chemistry, 5th Edition (1989) Longman Scientific & Technical, pp. 165-168, incorporated herein by reference. For example, suitable drying agents are anhydrous CaSO_4 , anhydrous Na_2SO_4 , calcium chloride, sodium sulfite and MgSO_4 . The selection of suitable drying agents may depend on the end use of the tablet. A drying agent for a detergent tablet for an automatic dishwashing composition for low temperatures preferably is sodium sulfite or calcium chloride, but anhydrous CaSO_4 , may be used for higher use temperatures. When present, drying agents are included in an amount of about 0.1% to about 15%, more preferably from about 0.1% to about 10%, even more preferably from about 0.5% to about 7%, by weight.

When the non-compressed, non-encapsulating portion is a gel mounted or formed onto the compressed solid body portion of the detergent tablet into a mould formed on the compressed solid body portion, the non-compressed, non-encapsulating portion may additionally contain a thickening system in addition to the at least one detergent active agent.

When the non-compressed, non-encapsulating portion is a gel it may include solid ingredients which are dispersed or suspended within the gel. The solid ingredients aid in the control of the viscosity of the gel formulation in conjunction with the thickening system. When included, the non-compressed, non-encapsulating portion typically comprises at least about 15% solid ingredients, more preferably at least about 30% solid ingredients and most preferably at least about 40% solid ingredients. However, due to pumpability and other processing concerns, the non-compressed, non-encapsulating portion of the present invention typically do not include more than about 90% solid ingredients, when in the form of a gel.

Thickening System

As noted earlier, the detergent tablet of the present invention comprises thickening system in the non-compressed, non-encapsulating portion when it is a gel, to provide the proper

viscosity or thickness of the gel portion. The thickening system typically comprises a non-aqueous liquid diluent and an organic or polymeric gelling additive

a) Liquid Diluent

The term "diluent" is used herein to connote the liquid portion of the thickening system.

- 5 While some of the essential and/or optional components of the compositions herein may actually dissolve in the "diluent"-containing phase, other components will be present as particulate material dispersed within the "diluent"-containing phase. Thus the term "diluent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto. Suitable types of diluent useful in the non-aqueous thickening systems herein include alkylene glycol mono lower alkyl ethers, propylene glycols, ethoxylated or
10 propoxylated ethylene or propylene, glycerol esters, glycerol triacetate, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

- A preferred type of non-aqueous diluent for use herein comprises the mono-, di-, tri-, or tetra- C₂-C₃ alkylene glycol mono C₂-C₆ alkyl ethers. The specific examples of such compounds
15 include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

- Another preferred type of non-aqueous diluent useful herein comprises the lower
20 molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

- Yet another preferred type of non-aqueous diluent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R¹-C(O)-OCH₃ wherein R¹
25 ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

- The non-aqueous organic diluent(s) employed should, of course, be compatible and non-reactive with other composition components, e.g., enzymes, used in the detergent tablets herein. Such a diluent component will generally be utilized in an amount of from about 10% to about
30 60% by weight of the composition. More preferably, the non-aqueous, low-polarity organic diluent will comprise from about 20% to about 50% by weight of the composition, most preferably from about 30% to about 50% by weight of the composition.

b) Gelling Additive

- As noted earlier, a gelling agent or additive is added to the non aqueous diluent of the
35 present invention to complete the thickening system. To form the gel required for suitable phase stability and acceptable rheology of the non-compressed, non-encapsulating portion, the organic

gelling agent is generally present to the extent of a ratio of diluent to gelling agent in thickening system typically ranging from about 99:1 to about 1:1. More preferably, the ratios range from about 19:1 to about 4:1.

The preferred gelling agents of the present invention are selected from castor oil derivatives, propylene glycol, polyethylene glycol, sorbitols and related organic thixotropes, organoclays, cellulose and cellulose derivatives, pluronics, stearates and stearate derivatives, sugar/gelatin combination, starches, glycerol, organic acid amides such as N-lauryl-L-glutamic acid di-n-butyl amide and mixtures thereof.

The preferred gelling agents are castor oil derivatives. Castor oil is a naturally occurring triglyceride obtained from the seeds of *Ricinus Communis*, a plant which grows in most tropical or subtropical areas. The primary fatty acid moiety in the castor oil triglyceride is ricinoleic acid (12-hydroxy oleic acid). It accounts for about 90% of the fatty acid moieties. The balance consists of dihydroxystearic, palmitic, stearic, oleic, linoleic, linolenic and eicosanoic moieties. Hydrogenation of the oil (e.g., by hydrogen under pressure) converts the double bonds in the fatty acid moieties to single bonds, thus "hardening" the oil. The hydroxyl groups are unaffected by this reaction.

The resulting hydrogenated castor oil, therefore, has an average of about three hydroxyl groups per molecule. It is believed that the presence of these hydroxyl groups accounts in large part for the outstanding structuring properties which are imparted to the non-compressed, non-encapsulating portion compared to similar liquid detergent compositions which do not contain castor oil with hydroxyl groups in their fatty acid chains. For use in the compositions of the present invention the castor oil should be hydrogenated to an iodine value of less than about 20, and preferably less than about 10. Iodine value is a measure of the degree of unsaturation of the oil and is measured by the "Wijis Method," which is well-known in the art. Unhydrogenated castor oil has an iodine value of from about 80 to 90.

Hydrogenated castor oil is a commercially available commodity being sold, for example, in various grades under the trademark CASTORWAX.RTM. by NL Industries, Inc., Highstown, New Jersey. Other Suitable hydrogenated castor oil derivatives are Thixcin R, Thixcin E, Thixatrol ST, Perchem R and Perchem ST, made by Rheox, Laporte. Especially preferred is Thixatrol ST.

Polyethylene glycols when employed as gelling agents, rather than solvents, have a molecular weight range of from about 2000 to about 30000, preferably about 4000 to about 12000, more preferably about 6000 to about 10000.

Cellulose and cellulose derivatives when employed in the present invention preferably include: i) Cellulose acetate and Cellulose acetate phthalate (CAP); ii) Hydroxypropyl Methyl Cellulose (HPMC); iii) Carboxymethylcellulose (CMC); and mixtures thereof. The

hydroxypropyl methylcellulose polymer preferably has a number average molecular weight of about 50,000 to 125,000 and a viscosity of a 2 wt. % aqueous solution at 25°C (ADTMD2363) of about 50,000 to about 100,000 cps. An especially preferred hydroxypropyl cellulose polymer is Methocel® J75MS-N wherein a 2.0 wt. % aqueous solution at 25°C. has a viscosity of about 75,000 cps.

The sugar may be any monosaccharide (e.g. glucose), disaccharide (e.g. sucrose or maltose) or polysaccharide. The most preferred sugar is commonly available sucrose. For the purposes of the present invention type A or B gelatin may be used, available from for example Sigma. Type A gelatin is preferred since it has greater stability in alkaline conditions in comparison to type B. Preferred gelatin also has a bloom strength of between 65 and 300, most preferably between 75 and 100.

The non-compressed, non-encapsulating portion of the present invention may include a variety of other ingredients in addition to the thickening agent as herein before described and the detergent active disclosed in more detail below. Ingredients such as perfumes and dyes may be included as well as swelling/adsorbing agents such as carboxymethylcelluloses and starches to aid in adsorption of excess diluent or aid in the dissolution or breakup of the non-compressed, non-encapsulating portion in the wash. In addition, hardness modifying agents may incorporated into the thickening system to adjust the hardness of the gel if desired. These hardness control agents are typically selected from various polymers and polyethylene glycol's and when included are typically employed in levels of less than about 20% and more preferably less than about 10% by weight of the solvent in the thickening system. For example, hardening agents, such as high molecular weight PEG, preferably of a molecular weight from 10,000 to 20,000 or possibly even higher molecular weight, can be added to decrease the hardening time of the non-compressed, non-encapsulating portion. Alternatively, water soluble polymeric materials such as of low molecular weight polyethylene glycols may be added to the mould to form an intermediate barrier layer prior to addition of the non-compressed, non-encapsulating portion when it is a gel. This speeds cooling and hardening of the gel by the melting/mixing of the water soluble polymeric material when the gel is added to the at least one mould. In addition, the intermediate layer may act as a barrier to prevent ingredients from the gel mixing or bleeding into the compressed portion.

Addition of an alkaline material, such as sodium or potassium hydroxide can also speed in hardening of the non-compressed, non-encapsulating portion when it is a gel. Preferably, these alkaline materials would be added to the mould before the addition of the gel. However, in alternative systems, the alkaline material may be added to the gel composition. These alkaline materials also have the advantage of acting as an additional alkalinity source that is discrete and would be slower dissolving and hence have a minimal impact on any effervescence system

present in the non-compressed, non-encapsulating portion yet provide an alkalinity boost in the wash.

When it is a gel the non-compressed, non-encapsulating portion of the present invention is formulated so that the gel is a pumpable, flowable gel at slightly elevated temperatures of around 30°C or greater to allow increased flexibility in producing the detergent tablet, but becomes highly viscous or hardens at ambient temperatures so that the gel is maintained in position in the at least one mould in the compressed solid body portion of the detergent tablet through shipping and handling of the detergent tablet. Such hardening of the non-compressed, non-encapsulating portion may be achieved, for example, by (i) by cooling to below the flowable temperature of the gel; (ii) by evaporation of the diluent; or by (iii) by polymerization of the gelling agent. Preferably, the gel portion is formulated such that the gel hardens to sufficiently so that the maximum force needed to push a probe into the dimple preferably ranges from about 0.5N to about 40N. This force may be characterized by measuring the maximum force needed to push a probe, fitted with a strain gauge, a set distance into the gel. The set distance may be between 40 and 80% of the total gel depth. This force can be measured on a QTS 25 tester, using a probe of 5mm diameter. Typical forces measured are in the range of 1N to 25N.

Additionally, it is preferred that when a 48 hour old tablet is inverted, at ambient conditions, for 10 minutes, more preferably 30 minutes, even more preferably 2 hours, the non-compressed, non-encapsulating portion does not drip or separate from the compressed solid body.

Lime soap dispersant compound - The compositions of detergent active components may contain a lime soap dispersant compound, preferably present at a level of from about 0.1% to about 40% by weight, more preferably about 1% to about 20% by weight, most preferably from about 2% to about 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. Preferred lime soap dispersant compounds are disclosed in PCT Application No. WO93/08877.

Material Care Agents - The preferred ADD compositions may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids as described in U.S. Patent Nos. 5,705,464, 5,710,115 and 5,646,101.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the ADD composition.

Other Materials - Detergent ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total,

from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as non-phosphate builders, chelants, enzymes, suds suppressors, dispersant polymers (e.g., from BASF Corp. or Rohm & Haas), color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, dyes, fillers, germicides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, perfumes, solubilizing agents, carriers, processing aids, pigments, and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101.

Since ADD compositions herein can contain water-sensitive ingredients or ingredients which can co-react when brought together in an aqueous environment, it is desirable to keep the free moisture content of the ADDs at a minimum, e.g., 7% or less, preferably 5% or less of the ADD; and to provide packaging which is substantially impermeable to water and carbon dioxide. Coating measures have been described herein to illustrate a way to protect the ingredients from each other and from air and moisture. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are another helpful means of assuring maximum shelf-storage stability. As noted, when ingredients are not highly compatible, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible multi-function components; however, the formulator prefers those materials which do not have a marked tendency to deposit or form films on dishes including those of plastic construction.

Product/Instructions - This invention also encompasses the inclusion of instructions on the use of the cleaning compositions described herein with the packages containing the cleaning compositions or with other forms of advertising associated with the sale or use of the cleaning compositions. The instructions may be included in any manner typically used by consumer product manufacturing or supply companies. Examples include providing instructions on a label attached to the container holding the composition; on a sheet either attached to the container or accompanying it when purchased; or in advertisements, demonstrations, and/or other written or oral instructions which may be connected to the purchase or use of the cleaning compositions.

Specifically the instructions will include a description of the use of the cleaning composition. The instructions, for instance, may additionally include information relating to the recommended amount of cleaning composition to apply to the surface, if soaking or rubbing is appropriate to the surface; the recommended amount of water, if any, to apply to the surface before and after treatment; other recommended treatment.

A product comprising a cleaning composition containing a multi-function component capable of hydrolyzing α -D-glucans, β -D-glucans and combinations, both physically and chemically, of α -D-glucans and β -D-glucans, as more fully described above, and optionally

containing an amylase, the product further including instructions for using the cleaning composition to clean a surface (fabric, dish, or other hard surface) in need of cleaning, the instructions including the step of contacting a surface with an effective amount of the cleaning composition such that said cleaning composition cleans said surface.

5 Process for Making Tablet

The detergent tablets of the present invention are prepared by separately preparing the composition of detergent active components forming the respective compressed portion and the non-compressed, non-encapsulating portion/s, forming the compressed solid body portion and delivering or adhering the non-compressed, non-encapsulating portion/s to the mould/s in the compressed portion.

The compressed portion is prepared by obtaining at least one detergent active component and optionally premixing with carrier components. Any pre-mixing will be carried out in a suitable mixer; for example a pan mixer, rotary drum, vertical blender or high shear mixer. Preferably dry particulate components are admixed in a mixer, as described above, and liquid components are applied to the dry particulate components, for example by spraying the liquid components directly onto the dry particulate components. The resulting composition is then formed into a compressed portion in a compression step using any known suitable equipment. Preferably the composition is formed into a compressed portion using a tablet press, wherein the tablet is prepared by compression of the composition between an upper and a lower punch. In a preferred embodiment of the present invention the composition is delivered into a punch cavity of a tablet press and compressed to form a compressed portion using a pressure of preferably greater than 6.3KN/cm^2 , more preferably greater than 9KN/cm^2 , most preferably greater than 14.4KN/cm^2 .

In order to form a tablet of the invention, wherein the compressed portion provides at least one mould to receive the non-compressed, non-encapsulating portion/s, the compressed portion is prepared using a modified tablet press comprising modified upper and/or lower punches. The upper and lower punches of the modified tablet press are modified such that the compressed portion provides one or more indentations which form the mould(s) to which the one non-compressed, non-encapsulating portion/s is delivered.

The compressed portion can be cooled or even frozen before the non-compressed, non-encapsulating portion/s are added to the at least one mould. This cooling or freezing is particularly beneficial when the non-compressed, non-encapsulating portion is a gel.

As described in detail herein before, the non-compressed, non-encapsulating portion/s comprises at least one detergent active component. The detergent active component and any other ingredients in the non-compressed, non-encapsulating portion/s are pre-mixed using any known suitable mixing equipment.

The non-compressed, non-encapsulating portion comprises at least one detergent active component. Where the non-compressed, non-encapsulating portion comprises more than one detergent active component the components are pre-mixed using any known suitable mixing equipment. In addition the non-compressed, non-encapsulating portion may optionally comprise a carrier with which the detergent active components are combined. The non-compressed, non-encapsulating portion may be prepared in solid or flowable form. Once prepared the composition is delivered to the compressed portion. The non-compressed, non-encapsulating portion may be delivered to the compressed portion by manual delivery or using a nozzle feeder extruder or by any other suitable means. As the compressed portion comprises a mould, the non-compressed, non-encapsulating portion is preferably delivered to the mould using accurate delivery equipment, for example a nozzle feeder, such as a loss in weight screw feeder available from Optima, Germany or an extruder.

Where the flowable non-compressed, non-encapsulating portion is in particulate form the process comprises delivering a flowable non-compressed, non-encapsulating portion to the compressed portion in a delivery step and then coating at least a portion of the non-compressed, non-encapsulating portion with a coating layer such that the coating layer has the effect of substantially adhering the non-compressed portion to the compressed portion.

Where the flowable non-compressed, non-encapsulating portion is affixed to the compressed portion by hardening, the process comprises a delivery step in which the flowable non-compressed, non-encapsulating portion is delivered to the compressed portion and a subsequent conditioning step, wherein the non-compressed, non-encapsulating portion hardens. Such a conditioning step may comprise drying, cooling, binding, polymerization etc. of the non-compressed, non-encapsulating portion, during which the non-compressed, non-encapsulating portion becomes solid, semi-solid or highly viscous. Heat may be used in a drying step. Heat, or exposure to radiation may be used to effect polymerization in a polymerization step.

It is also envisaged that the compressed portion may be prepared having a plurality of moulds. The plurality of moulds are then filled with a non-compressed, non-encapsulating portion. It is also envisaged that each mould can be filled with a different non-compressed, non-encapsulating portion or alternatively, each mould can be filled with a plurality of different non-compressed, non-encapsulating portion.

The detergent tablets may be employed in any conventional domestic washing process wherein detergent tablets are commonly employed, including but not limited to automatic dishwashing and fabric laundering.

Methods of Cleaning

The surface in need of treatment is preferably selected from the group consisting of stainless steel and other metals, ceramic, plastic, metal, dishware, cookware, baby bottles, wood, glass and mixtures thereof. Such surfaces can be either non-porous or porous.

The method herein when employed to remove or reduce soils or stains is highly effective on cooked-on, burned-on, dried-on and baked-on food soils. Additionally, it is highly effective on starch soils such as oatmeal and macaroni soils.

The cleaning compositions of the present invention are effective immediately upon contacting the soils and/or stains. However, the cleaning compositions are preferably in contact with the soils and/or stains for a period of about 1 to about 120 minutes, more preferably, about 5 to about 60 minutes, most preferably, about 10 to about 30 minutes (the typical wash cycle time for automatic dishwashing machines).

The cleaning compositions of the present invention are suitable for use at any temperature at which the multi-function components that are capable of hydrolyzing both 1-3- β -D-glucans and 1-4- β -D-glucans are effective. Preferably, the cleaning compositions are used at temperatures below about 70°C, more preferably, below about 60°C, most preferably, below about 50°C.

Preferred multi-function components that are capable of hydrolyzing both 1-3- β -D-glucans and 1-4- β -D-glucans include, but are not limited to, enzymes, more preferably cellulases.

The dishwashing methods of the present invention comprise contacting a surface in need of treatment with an effective amount of a cleaning composition containing a multi-function component that is capable of hydrolyzing both 1-3- β -D-glucans and 1-4- β -D-glucans such that the cleaning composition treats the surface. Preferably, the cleaning compositions of the present invention are used in automatic dishwashers. However, in the case of manual dishwashing, any friction between the surface and the cleaning composition, such as by scrubbing, etc., will facilitate removal and/or reduction of the soils. Although the methods and cleaning compositions of the present invention can be employed to assist in cleaning, especially tough food cleaning and/or removing and/or reducing spotting and/or films, surfaces in need of treatment for any desired purpose, examples of likely uses include one or more of the following: soil removal, soil reduction, spot and/or film removal and/or reduction, grit removal, filter cleaning, stain removal and stain reduction. Preferably, the soils are carbohydrate soils, such as cellulose, gluon and xylon substrates derived from cereal and grain soils. More preferably, the soils are oatmeal, barley, rye, wheat, rice and mixtures thereof.

Any suitable methods for machine washing or cleaning soiled tableware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, silverware, metallic items, cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a detergent tablet in accord

with the invention. By an effective amount of the detergent tablet it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods. Preferably the detergent tablets are from 15g to 40g in weight, more preferably from 20g to 35g in weight.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

Cleaning Compositions for Hard Surfaces and Dishes Examples

The abbreviations and terms used in the Examples are known to those of ordinary skill in the art and/or are defined herein.

Hard surface cleaning compositions

As used herein "hard surface cleaning composition" refers to liquid and granular detergent compositions for cleaning hard surfaces such as floors, walls, bathroom tile, and the like. Hard surface cleaning compositions of the present invention comprise an effective amount of one or more protease enzymes, preferably from about 0.0001% to about 10%, more preferably from about 0.001% to about 5%, more preferably still from about 0.001% to about 1% by weight of active protease enzyme of the composition. In addition to comprising one or more protease enzymes, such hard surface cleaning compositions typically comprise a surfactant and a water-soluble sequestering builder. In certain specialized products such as spray window cleaners, however, the surfactants are sometimes not used since they may produce a filmy/streaky residue on the glass surface. (See U.S. Patent No. 5,679,630 Examples).

The surfactant component, when present, may comprise as little as 0.1% of the compositions herein, but typically the compositions will contain from about 0.25% to about 10%, more preferably from about 1% to about 5% of surfactant.

Typically the compositions will contain from about 0.5% to about 50% of a detergency builder, preferably from about 1% to about 10%. Preferably the pH should be in the range of about 8 to 12. Conventional pH adjustment agents such as sodium hydroxide, sodium carbonate or hydrochloric acid can be used if adjustment is necessary.

Solvents may be included in the compositions. Useful solvents include, but are not limited to, glycol ethers such as diethyleneglycol monohexyl ether, diethyleneglycol monobutyl ether, ethyleneglycol monobutyl ether, ethyleneglycol monohexyl ether, propyleneglycol monobutyl ether, dipropyleneglycol monobutyl ether, and diols such as 2,2,4-trimethyl-1,3-pentanediol and 2-ethyl-1,3-hexanediol. When used, such solvents are typically present at levels of from about 0.5% to about 15%, preferably from about 3% to about 11%.

Additionally, highly volatile solvents such as isopropanol or ethanol can be used in the present compositions to facilitate faster evaporation of the composition from surfaces when the

surface is not rinsed after "full strength" application of the composition to the surface. When used, volatile solvents are typically present at levels of from about 2% to about 12% in the compositions.

The hard surface cleaning composition embodiment of the present invention is illustrated by the following nonlimiting examples.

Examples 1-7

Liquid Hard Surface Cleaning Compositions

		Example No.						
Component		1	2	3	4	5	6	7
10	Endoglucanase ¹ (pure)	0.05	0.05	0.20	0.02	0.03	0.10	0.03
	Amylase ²	0.36	-	-	0.42	-	0.36	-
	Chelant**	-	-	-	2.90	2.90	-	-
	Citrate	-	-	-	-	-	2.90	2.90
	LAS	-	1.95	-	1.95	-	1.95	-
15	AS	2.00	-	2.20	-	2.20	-	2.20
	AES	2.00	-	2.20	-	2.20	-	2.20
	Amine Oxide	0.40	-	0.50	-	0.50	-	0.50
	Hydrotrope	-	1.30	-	1.30	-	1.30	-
	Solvent***	-	6.30	6.30	6.30	6.30	6.30	6.30
20	Water and Minors	balance to 100%						

¹ Endoglucanase having the amino acid sequence SEQ ID No. 1.

² Amylase as described in WO 95/26397 and WO 96/23873.

**Na₄ ethylenediamine diacetic acid

***Diethyleneglycol monohexyl ether

25 ****All formulas adjusted to pH 7

Dishwashing Compositions

EXAMPLE 8

A detergent tablet according to the present invention may be prepared as follows. A detergent composition as in Example 2, formulation A is prepared and passed into a conventional rotary press. The press includes one punch shaped so that a mould is formed into one of the tablet surfaces. A gel matrix formulation as disclosed in Example 2, formulation A is then prepared. The proper amount of non-aqueous solvent is provided to a mixer and shear is applied to the solvent at a moderate rate (2,500-5,000 rpm). The proper amount of gelling agent is gradually added to the solvent under shear conditions until the mixture is homogeneous. The shear rate of the mixture is gradually increased to high shear condition of around 10,000 rpm.

The temperature of the mixture is increased to between 55°C and 60°C. The shear is then stopped and the mixture is allowed to cool to temperatures between 35°C and 45°C. Using a low shear mixer, the remaining ingredients are then added to the mixture as solids. The final mixture is then metered into the mould on the compressed tablet body and allowed to stand until the gel hardens or is no longer flowable.

EXAMPLE 9

Automatic dimple tablet dishwashing detergent formulations in accordance with the present invention are prepared as follows:

10

	g/tab	g/tab	g/tab	g/tab	g/tab
Dimple					
Citric acid	0.3	0.6	0.6	0.6	0.3
Bicarbonate	0.88	0.6	0.6	0.6	0.88
PEG (+0.0015 g Sandolan EHRL)	0.14	-	-	-	0.14
PEG 6000	-	0.17	0.17	0.17	-
Triacetin	-	1.21	1.21	1.21	-
Calcium Chloride	0.07	0.13	0.13	0.13	0.07
Endoglucanase ¹ (pure)	0.10	0.15	0.20	0.30	0.30
Amylase ²	0.36	0.42	0.42	0.42	0.36
Protease ³	0.25	0.33	0.33	0.33	0.25
Dimple Total	2.1	3.61	3.66	3.76	2.3
Tablet Body					
Sodium Carbonate	2.33	3.5	5.25	5.25	3.59
STPP(12% H2O)	9.62	-	9.93	9.93	9.57
STPP(8% H2O A&W)	-	10.1	-	-	-
Granular HEDP	0.18	0.18	0.28	0.28	0.28
2 r Silicate	0.5	1.1	1.65	1.65	1.0
SKS 6	1.5	1.5	2.25	2.25	2.3
Amylase ⁴	0.112	0.15	0.225	0.225	-
Amylase ⁵	-	-	-	-	0.255
Amylase ⁶	0.038	-	-	-	-
Protease ⁷	0.06	0.12	0.18	0.18	0.09

Perborate	2.45	2.8	4.2	4.2	3.66
Plurafac ⁸	0.4	-	-	0.9	1.2
C18	-	0.665	0.9975	-	-
ACN ⁹	-	0.135	0.2025	-	-
PEG 4000	0.4	0.26	0.39	0.39	0.38
BTA	0.04	-	-	-	-
Winog (paraffin-oil)	0.1	0.1	0.15	0.15	0.16
Perfume	0.02	0.022	0.013	0.013	0.013
Sulfate	-	-	-	-	0.50
Tablet Body Total	17.75	20.632	25.72	25.42	22.998
Total Tablet	19.85	24.24	29.4	29.2	25.298

¹ Endoglucanase having the amino acid sequence SEQ ID No. 1.

² Amylase as described in WO 95/26397 and WO 96/23873.

³ Protease as disclosed in U.S. Patent No. 5,677,272.

⁴ Termamyl[®] 2xPCA commercially available from Novo Nordisk A/S.

5 ⁵ Termamyl[®] 1xPCA commercially available from Novo Nordisk A/S.

⁶ White Termamyl[®] commercially available from Novo Nordisk A/S.

⁷ Savinase[®] commercially available from Novo Nordisk A/S.

⁸ Plurafac C₁₃-C₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename

10 Plurafac by BASF.

⁹ Alkyl-capped nonionic surfactant.

EXAMPLE 10

Automatic dimple tablet dishwashing detergent formulations in accordance with the present
15 invention are prepared as follows:

	g/tab	g/tab	g/tab	g/tab	g/tab
Dimple					
Citric acid	0.23	0.23	0.60	0.23	0.23
Bicarbonate	0.59	0.59	0.6	0.59	0.59
Sandolan EHRL Dye	0.0017	0.0017	0.0013	0.0017	0.0017
PEG 6000	-	-	0.17	-	-
PEG 4000	0.08	0.08	-	0.08	0.08

PEG 400	0.02	0.02	-	0.02	0.02
Triacetin	-	-	1.21	-	-
Calcium Chloride	-	-	0.13	-	-
Endoglucanase ¹ (pure)	0.10	0.3	0.20	0.10	0.30
Amylase ²	0.32	0.32	0.42	0.32	0.32
Protease ³	0.27	0.27	0.33	0.27	0.27
Dimple Total	1.6	1.8	3.66	1.6	1.8
Tablet Body					
Sodium Carbonate	3.5	3.5	2.8	5.25	5.25
STPP(12% H2O)	10.6	-	10.6	10.34	-
STPP(8% H2O A&W)	-	10.1	-	-	9.50
Blue STPP Speckle	-	-	-	-	-
Granular HEDP	0.18	0.18	0.18	0.28	0.28
2 r Silicate	1.6	1.1	0.7	2.4	1.65
Meta Silicate	-	-	2.2	-	-
SKS 6	1.5	1.5	-	2.25	2.25
Amylase ⁴	0.11	0.11	0.15	0.17	0.17
Amylase ⁶	-	-	-	-	-
Protease ⁷	0.12	0.12	0.12	0.18	0.18
Protease ³	-	-	-	-	-
Perborate	2.45	2.45	2.8	3.68	3.68
Plurafac ⁸	0.8	0.6	0.4	1.2	0.9
PEG 4000	0.26	-	-	0.39	-
PEG 6000	-	0.26	-	-	0.39
BTA	0.06	0.06	0.06	0.09	0.09
Winog (paraffin oil)	0.1	0.1	0.1	0.15	0.15
Perfume	0.02	0.02	0.02	0.01	0.01
Tablet Body Total	21.3	20.1	20.13	26.4	24.5
Total Tablet	22.9	21.9	23.79	28.0	26.3

¹ Endoglucanase having the amino acid sequence SEQ ID No. 1.

² Amylase as described in WO 95/26397 and WO 96/23873.

³ Protease as disclosed in U.S. Patent No. 5,677,272.

⁴ Termamyl® 2xPCA commercially available from Novo Nordisk A/S.

⁶ White Termamyl[®] commercially available from Novo Nordisk A/S.

⁷ Savinase[®] commercially available from Novo Nordisk A/S.

⁸ Plurafac C₁₃-C₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename

5 Plurafac by BASF.

Example 11

The following formulations are examples of compositions in accordance with the invention, which may be in the form of granules or in the form of a tablet.

10

Component	
Base Product	
C45 AS/TAS	3.0
LAS	8.0
C25AE3S	1.0
NaSKS-6	9.0
C25AE5/AE3	5.0
Zeolite A	10.0
SKS-6 (I) (dry add)	2.0
MA/AA	2.0
Citric acid	1.5
EDDS	0.5
HEDP	0.2
PB1	10.0
NACA OBS	2.0
TAED	2.0
Carbonate	8.0
Sulfate	2.0
Endoglucanase ¹	0.1
Amylase ²	0.3
Lipase	0.2
Protease ³	0.02
Minors (Brightener/SRP1/ CMC/Photobleach/ MgSO4/	0.5

PVPVI/Suds suppressor/ PEG)	
Perfume	0.5

¹ Endoglucanase having the amino acid sequence SEQ ID No. 1.

² Amylase as described in WO 95/26397 and WO 96/23873.

³ Protease as disclosed in U.S. Patent No. 5,677,272.

5 While particular embodiments of the subject invention have been described, it will be obvious to those skilled in the art that various changes and modifications of the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the invention.

10 Having described the invention in detail with reference to preferred embodiments and the examples, it will be clear to those skilled in the art that various changes and modifications may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. A cleaning composition comprising
 - 5 a) a multi-function component that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans; and
 - b) one or more cleaning adjunct materials selected from the group consisting of: low foaming nonionic surfactants, hydrotropes and mixtures thereof.
- 10 2. The cleaning composition according to Claim 1 wherein said multi-function component is a cellulase enzyme, preferably an endoglucanase (EC 3.2.1.4), more preferably an endoglucanase (EC 3.2.1.4) which exhibits the following properties:
 - 15 (a) derived from *Humicola insolens*, DSM 1800;
 - (b) approximate molecular weight of 50 kDa;
 - (c) iso-electric point of 5.5; and
 - (d) containing 415 amino acids;or an endoglucanase (EC 3.2.1.4) that has the amino acid sequence SEQ ID No. 1.
- 20 3. The cleaning composition according to Claim 1 wherein said cleaning composition further comprises an amylase, preferably an α -amylase variant selected from the group consisting of:
 - (i) α -amylase characterized by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the
25 range of 8 to 10, measured by Phadebas[®] α -amylase activity assay and/or;
 - (ii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID No. 2 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 2 and/or;
 - (iii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID
30 No. 3 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 3 and/or;
 - (iv) α -amylase according to (i) comprising the following amino acid sequence N-terminal: His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp (SEQ ID No. 4) or an α -amylase being at least 80% homologous with the amino acid
35 sequence shown (SEQ ID No. 4) in the N-terminal and/or;

(v) α -amylase according to (i-iv) wherein the α -amylase is obtainable from an alkalophilic *Bacillus* species and/or;

(vi) α -amylase according to (v) wherein the α -amylase is obtainable from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935 and/or;

5 (vii) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to SEQ ID No. 2, ID No. 3, or ID No. 4 and/or; _____

(viii) variant of a parent α -amylase, wherein the parent α -amylase (1) has one of the amino acid sequences shown in SEQ ID No. 2, ID No. 3, or ID No. 4, respectively, or (2) displays
10 at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequences, in which variants: (A) at least one amino acid residue of said parent α -amylase has been deleted;
15 and/or (B) at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or (C) at least one amino acid residue has been inserted relative to said parent α -amylase; said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase: increased thermostability; increased stability towards oxidation; reduced Ca ion dependency; increased stability and/or α -amylolytic
20 activity at neutral to relatively high pH values; increased α -amylolytic activity at relatively high temperature; and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.

4. The cleaning composition according to Claim 3 wherein said multi-function component
25 and amylase are present in said cleaning composition in a range of ratios by ppm from 20:1 to 1:20, preferably from 10:1 to 1:10, more preferably from 3:1 to 1:3.

5. The cleaning composition according to any of the preceding Claims wherein said cleaning adjunct materials further comprise one or more other surfactants, solvents, buffers, other
30 enzymes, soil release agents, clay soil removal agents, thickeners, builders, dispersing agents, bleaching agents, baking soda, carbonates, phosphates, suds suppressors, fabric softening agents, chelants, dyes, hydrobenzoic acid, dicarboxylic acid, siloxanes, perfumes, water and mixtures thereof, preferably wherein said cleaning adjunct materials further comprise a branched surfactant.

35

6. The cleaning composition according to Claim 5 wherein said cleaning adjunct materials further comprise at least 0.1% surfactant by weight of the composition, said surfactant comprising materials selected from the group consisting of alkyl benzene sulfonates, primary alkyl sulfates, secondary alkyl sulfates, alkyl alkoxy sulfates, alkyl alkoxy carboxylates, alkyl polyglycosides and their corresponding sulfated polyglycosides, α -sulfonated fatty acid esters, alkyl and alkyl phenol alkoxyates, betaines and sulfobetaines amine oxides, N-methyl-glucamides, nonionic primary alcohol ethoxylates, nonionic primary alcohol mixed ethoxy/propoxy, and mixtures thereof, preferably further comprising at least 5% builder selected from the group consisting of zeolites, polycarboxylates, layered silicates, phosphates, and mixtures thereof.
7. The cleaning composition according to Claim 5 wherein said cleaning adjunct materials further comprise at least one bleaching agent selected from the group consisting of percarbonates, perborate, and mixtures thereof, preferably further comprising at least one bleach activator selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C₁₀-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C₈-OBS), perhydrolyzable esters, 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS), lauryloxybenzenesulphonate (LOBS or C₁₂-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C₁₁-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA) and mixtures thereof.
8. The cleaning composition according to Claim 5 wherein said cleaning adjunct materials further comprise at least one other deterative enzyme selected from the group consisting of other cellulases, lipases, other amylases, phospholipases, proteases, peroxidases and mixtures thereof.
9. The cleaning composition according to Claim 1 wherein said cleaning composition is in the form of a liquid, granule or bar.
10. The cleaning composition according to any of Claims 1-8 wherein said cleaning composition is a dishwashing detergent composition comprising:
- (a) from 0.0001% to 10% by weight of the composition of said multi-function component; and
 - (b) from 0.1% to 10% by weight of the composition of said low foaming nonionic surfactant; and

(c) optionally, from 0.5% to 20% by weight of the composition of a bleaching agent.

11. The cleaning composition according to Claim 10 wherein said dishwashing detergent composition is in the form of a liquid, granule, powder or tablet.

12. An automatic dishwashing composition comprising:

(a) a tablet body including one or more cleaning adjunct materials; and

(b) a dimple portion including a multi-function component capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations, both physically and chemically, of 1,3- β -glucans and 1,4- β -glucans;

wherein said dimple portion is attached to said tablet body such that said multi-function component is capable of activation prior to activation of said one or more cleaning adjunct materials of said tablet body.

13. A method for cleaning a surface in need of cleaning comprising contacting said surface with the dishwashing detergent composition according to Claim 10.

14. A method according to Claim 13 wherein said surface is selected from the group consisting of stainless steel, other metal substrates, ceramic, plastic, dishware, cookware, baby bottles, wood, glass, and mixtures thereof.

15. The method according to Claim 13 wherein said surface is treated for soil removal and/or soil reduction, preferably wherein the soil is a carbohydrate soil.

16. The method according to Claim 13 wherein said cleaning composition is formulated for activation of said multi-function component prior to activation of said one or more cleaning adjunct materials.

17. The method according to Claim 13 wherein said cleaning composition is an automatic dishwashing composition.

18. Use of the cleaning composition according to any of Claims 1-11 to clean a surface in need of cleaning.

19. A surface cleaned by the method according to Claim 13.

20. A dishwashing product comprising a cleaning composition containing a multi-function component capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically-linked 1,3- β -glucans and 1,4- β -glucans, and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, said product further including instructions for using said cleaning composition, the instructions including the step of contacting a surface in need of cleaning with an effective amount of said cleaning composition such that said cleaning composition cleans said surface.
- 10 21. The product of Claim 20 wherein said multi-function component is an endoglucanase (EC 3.2.1.4), preferably an endoglucanase (EC 3.2.1.4) which exhibits the following properties:
- (a) derived from *Humicola insolens*, DSM 1800;
 - (b) approximate molecular weight of 50 kDa;
 - (c) iso-electric point of 5.5; and
 - 15 (d) containing 415 amino acids
- or an endoglucanase (EC 3.2.1.4) having the amino acid sequence SEQ. ID No. 1.
22. The product of Claim 20 wherein said cleaning composition further includes an amylase.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 July 2000 (20.07.2000)

PCT

(10) International Publication Number
WO 00/41522 A3

(51) International Patent Classification⁷: **C11D 3/386**,
17/00

4HE (GB). SPEED, Lynda, Anne [US/GB]; 21 Mayfield
Road, Gosforth, Newcastle Upon Tyne NE3 4HE (GB).

(21) International Application Number: **PCT/US00/00437**

(74) Agents: **REED, T., David et al.**; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

(22) International Filing Date: 7 January 2000 (07.01.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/115,379 11 January 1999 (11.01.1999) US

(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, EE, FI, GB, GD, GE, GH, GM, HR, HU, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:
7 September 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BETTIOL, Jean-Luc, Philippe** [FR/GB]; 8 East Avenue, Benton, Newcastle Upon Tyne NE12 9PH (GB). **ZHU, Yong** [CN/US]; 4348 Bromyard Avenue, Cincinnati, OH 45241 (US). **WELLS, Eric, Christopher** [US/US]; 1440 West Kemper Road, Cincinnati, OH 45240 (US). **SHOWELL, Michael, Stanford** [US/US]; 685 Compton Road, Cincinnati, OH 45231 (US). **CONVENTS, Andre, Christian** [US/US]; 9696 Humphrye Road, Cincinnati, OH 45242 (US). **THOEN, Christiaan, Arthur, Jacques, Kamiel** [BE/US]; 8485 Rupp Farm Drive, West Chester, OH 45069 (US). **WARD, Glenn, Steven** [US/GB]; 3 Willerby Drive, Whitebridge Park, Gosforth, Newcastle Upon Tyne NE3

(54) Title: **CLEANING COMPOSITIONS CONTAINING A MULTI-FUNCTION COMPONENT AND METHOD FOR USING**

(57) Abstract: The present invention relates to cleaning compositions comprising a multi-function component that is capable of hydrolyzing 1,3- β -glucans, 1,4- β -glucans and combinations of both physically and chemically linked 1,3- β -glucans and 1,4- β -glucans, and one or more cleaning adjunct materials selected from the group consisting of low foaming nonionic surfactants, hydrotropes and mixtures thereof, and methods for using the cleaning compositions for cleaning, especially tough food cleaning, or otherwise removing and/or reducing soils, especially carbohydrate soils, and/or removing or reducing spotting and films, from dishware, cookware and other hard surface substrates.

WO 00/41522 A3

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 00/00437

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, STRAND, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 02675 A (PROCTER & GAMBLE) 26 January 1995 (1995-01-26) cited in the application	1-9, 18
Y	claims 1,8-13,16,17,20-24,29-36	1,3
A	page 23, line 22 -page 24, line 30 page 38, line 29 - line 33	10,11
Y	WO 95 26397 A (NOVONORDISK AS) 5 October 1995 (1995-10-05) cited in the application claims 1-18 examples 4-6 page 12, line 17 -page 30, line 26 -/--	1,3

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

18 July 2000

Date of mailing of the international search report

25/07/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Neys, P

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PCT/US 00/00437

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 23873 A (NOVONORDISK AS) 8 August 1996 (1996-08-08) cited in the application claims 1-11, 19-28 page 36, line 21 -page 58, line 4 ---	1, 3
P, A	WO 99 27063 A (PROCTER & GAMBLE) 3 June 1999 (1999-06-03) page 54, line 9 -page 55, line 27 claims -----	1, 10-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/US 00/00437

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9502675 A	26-01-1995	AU 7069294 A	13-02-1995
		BR 9407066 A	12-03-1996
		CN 1129011 A	14-08-1996
		CZ 9600110 A	12-06-1996
		EG 20618 A	30-09-1999
		EP 0708819 A	01-05-1996
		FI 960132 A	11-03-1996
		JP 9500667 T	21-01-1997
WO 9526397 A	05-10-1995	AU 2067795 A	17-10-1995
		BR 9507229 A	16-09-1997
		CA 2186592 A	05-10-1995
		CN 1144538 A	05-03-1997
		EP 0753057 A	15-01-1997
		FI 963861 A	27-09-1996
		JP 9510617 T	28-10-1997
		US 5824531 A	20-10-1998
		US 5856164 A	05-01-1999
		ZA 9502565 A	21-12-1995
WO 9623873 A	08-08-1996	AU 4483396 A	21-08-1996
		BR 9607735 A	14-07-1998
		CA 2211405 A	08-08-1996
		CN 1172500 A	04-02-1998
		EP 0815208 A	07-01-1998
		JP 11503003 T	23-03-1999
WO 9927063 A	03-06-1999	BR 9807007 A	14-03-2000
		DE 29823751 U	13-01-2000
		EP 0973862 A	26-01-2000
		ES 2142783 T	01-05-2000

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